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SINTERING OF SUPPORTED METAL CATALYSTS: COMPARISON OF DIFFERENT METALS AND SUPPORTS

BY

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled SINTERING OF SUPPORTED METAL CATALYSTS: COMPARISON OF DIFFERENT METALS AND SUPPORTS submitted by Bharat S. Chahar, B. Tech., in partial fulfilment of the requirements for the degree of Master of Science.

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DEDICATION

I would like to dedicate this thesis to my parents, who despite being more than ten thousand miles away, were a continuous source of inspiration and encouragement, and without whose love and affection, this work would not have been possible.

ABSTRACT

The sintering behavior of various supported metal catalysts was studied. The relative stabilities of various metals (Pt, Ir and Rh) supported on the same support (alumina) and platinum supported on various supports (γ-alumina, silica-alumina and silica gel) were compared after thermal treatments in oxygen and hydrogen atmospheres at temperatures of $\leq$ 800°C. The sintering behavior of these catalysts was studied for treatment times of 1, 4 and 16 hours at various temperatures.

The changes in metal dispersion during thermal treatments were used to compare the stabilities of the various catalysts. The dispersions were measured for unsintered and sintered catalyst samples by hydrogen chemisorption. The pulse dynamic adsorption method was employed for measuring hydrogen adsorption uptakes. The effects of thermal treatment on support crystalline structure and support surface area were studied by X-ray diffraction and BET surface area measurements.

In oxygen atmospheres the sequence of thermal stability for the different supported metals studied was found to be Rh > Pt > Ir, while in hydrogen atmospheres the sequence was Ir > Rh > Pt. Increases in dispersions due to treatment in oxygen were observed for Pt and Ir catalysts. The relative stabilities for supported Pt catalysts on different supports was found to be Pt/γ-alumina > Pt/silica-alumina $\geq$ Pt/silica gel in both hydrogen and oxygen atmospheres.

The observed relative stabilities were compared to qualitative predictions based on sintering mechanisms. The crystallite migration mechanism is unable to explain the observed results for

sintering in oxygen. The results are in agreement with predictions of the atomic migration mechanism. It was concluded that the crystallite migration mechanism is not the main mechanism for sintering of supported metal catalysts in oxygen. Further experimentation is necessary to confirm the belief that the atomic migration mechanism is also the predominant mechanism for sintering of supported metal catalysts in hydrogen atmospheres.

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CHAPTER 1

INTRODUCTION

1.1 Supported Metal Catalysts

Metal catalysts are one of the key ingredients in many chemical processes. Processes such as hydrocarbon hydrogenation and dehydrogenation, petroleum reforming, isomerization and partial oxidation use these catalysts. But, supported metal catalysts, rather than bulk metal catalysts, are usually used because of the high cost and short life of bulk metal catalysts.

Supported metal catalysts consist of an active metal (*e.g.* Pt, Pd, Ru, Rh, and Ir) supported on a relatively stable and high surface area support (*e.g.* alumina, silica, and molecular sieves). The metal in supported metal catalysts is present as small crystallites (usually < 5 nm in diameter in fresh catalysts) distributed over the surface of the support. Because of the small size of the crystallites, a large fraction of the total metal atoms are surface metal atoms. The ratio of surface metal atoms to the total metal atoms is called the dispersion, and the high dispersion of supported metal catalysts is one of the reasons for their extensive use. For example, a supported platinum catalyst with an average crystallite size of 2 nm has a dispersion of ~0.5, while a bulk platinum powder with an average particle size of 2.0 mm has a dispersion of $\sim 5 \times 10^{-7}$. This means that in the above example, utilization of the platinum as a catalyst in the supported metal catalyst is one million times greater than that of the powder because the catalytic activity is usually approximately proportional to the metal surface area.

Another reason for the use of the supported metal rather than bulk metal catalysts is the superior thermal stability of the supported metal catalysts. In bulk metal catalysts the metal particles are in direct physical contact with each other and exposure of the bulk metal powder to elevated temperatures ($\geq$ 150°C) causes fusion of the particles resulting in a loss in surface area. In supported metal catalysts, the small metal crystallites are physically separated on the support surface and the metal crystallites are stable to significantly higher temperatures.

The technique most commonly employed to prepare supported metal catalysts is impregnation. It consists of contacting the support with an aqueous solution containing a salt of the desired metal and then evaporating the water. This results in the precipitation of the metal salt onto the support surface. Treatment in a reducing atmosphere results in formation of the small metal crystallites. Often the freshly impregnated catalyst is calcined in air, converting the metal salt into metal oxide. The metal oxide is then reduced to zero valent metal prior to using the catalyst.

1.2 Sintering of Supported Metal Catalysts

Despite being more stable than bulk metal catalysts, the activity of supported metal catalysts decreases after prolonged exposure to high temperatures. This loss in activity is due to an increase in the average metal crystallite size, *i.e.* a decrease in metal surface area. The process by which this crystallite growth occurs is known as sintering. The sintering behaviour of a particular catalyst is important in evaluating the catalyst performance. Sintering rates are influenced by various factors, but for a given catalyst, temperature, sintering

atmosphere and length of exposure to elevated temperatures are the main factors.

A considerable amount of theoretical modelling on the sintering of supported metal catalysts has been done in the past few years, but very little experimental data are available to discriminate among the various proposed sintering models. In the present work, the influence on the sintering behaviour in oxidizing and reducing atmospheres of different metals on one support (Al_2O_3) and of one metal (Pt) on various supports was studied. The results of this work are compared to qualitative predictions of various previously proposed mechanistic models.

CHAPTER 2

LITERATURE SURVEY ON SINTERING OF SUPPORTED METAL CATALYSTS

2.1 Introduction

The thermal stability of supported metal catalysts has been the focal point of study for a number of investigators in the past two decades. Some workers obtained experimental data and possible correlation among the data, while others attempted to formulate a mechanism for sintering which would fit the available data. The first part of this chapter briefly reviews the experimental data on sintering and the second part gives a brief description of the main mechanistic models that have been developed.

2.2 Experimental Investigations

2.2.1 Experimental Data

There are few experimental studies reported in the literature which are systematic enough to determine the effects of the many variables, such as time, temperature and type of atmosphere, on the sintering rate of a particular catalyst. Also, in many cases, it is very difficult to compare data of one worker with another because of differences in pretreatment conditions and different techniques used to measure catalytic activity.

Among the earlier studies on sintering, the work of Hermann *et al.* (1) and Maat and Moscou (2) is cited very frequently. Hermann *et al.* determined the sintering behavior of Pt on γ-alumina catalysts in nitrogen at temperatures from 560°C to 625°C with treatment times of 4 to 350 hours. Maat and Moscou (2) repeated the same kind of experiments at 780°C in air. The catalyst samples used in these experiments

were not reduced properly prior to hydrogen chemisorption. Dispersions were measured by chemisorbing hydrogen at 200°C. They concluded that rate of sintering in nitrogen follows a second order rate kinetics.

Mills *et al.*(3) carried out experiments on the sintering of 0.5% Pt on γ-alumina in air, hydrogen and steam and found that catalytic activity of samples decreased after treatment in air and hydrogen above 600°C. In the presence of small amounts of steam during sintering, the activity increased slightly, but decreased drastically when the sample was sintered in pure steam at 482°C. The catalytic activity was measured by a dehydrogenation reaction (conversion of cyclohexane to benzene). The results are very difficult to interpret because of the unconventional treatment procedure used.

Adler and Keavney (4) also studied the sintering of Pt on γ-alumina in steam and air mixtures at 705°C and they also found that as the partial pressure of steam increases, the rate of sintering increases. However, the catalyst used in this study was not reduced completely before hydrogen adsorption measurements.

Johnson and Keith (5) found that dispersion of a deactivated commercial Pt /Al_2O_3 catalyst increased when treated in air at temperatures between 440°C and 500°C, followed by a reduction in hydrogen at 482°C for 4 hours. They attributed this increase due to Pt O_2-alumina complex formation. They also observed that increasing the oxygen partial pressure resulted in higher dispersions. Carbon monoxide chemisorption was used to measure the changes in dispersion. The patent literature also describes a process for the regeneration of deactivated supported metal catalyst by treating them at about 500°C in an oxygen containing atmosphere (6). Other studies reporting redispersion are discussed later.

Benesi *et al.*(7) reported the effect of preparation method on thermal stability on silica supported catalysts. They compared the loss of metal area for 'impregnated' and 'ion exchanged' 1.6% Pt / SiO_2 catalysts. It was found that impregnated catalyst lost 39% of its metal surface area due to sintering during a 2 hour treatment in hydrogen at 800°C, while the catalyst prepared by ion exchange method lost 31% of initial dispersion for the same treatment. But it was observed that silica gel itself undergoes a 20% loss in surface area upon being heated to 800°C. In that case major part of the loss in platinum area would have occured through occlusion of platinum crystallites situated in the regions of the collapsed silica gel structure.

Wilson and Hall (8, 9) have done studies on stoichiometry of hydrogen chemisorption on Pt, for Pt/alumina Pt/silica and Pt/zeolite catalysts. They observed that for Pt/alumina and Pt/silica catalysts, H:Pt ratio is close to 1, but it is difficult to conclude the same for Pt/zeolite. They also studied sintering of these catalysts in hydrogen and found that Pt/silica loses its activity at a faster rate than Pt/alumina between 550°C and 770°C.

Sagert and Pouteau (10) studied the effect of sintering 1% Pt on silica gel in air from 400°C to 700°C. No significant redispersion was observed in this case. Some workers reporting significant redispersion of Pt on alumina have already been mentioned (4, 5, 6). Jaworska-Galas and Wrzyszcz (11) reactivated a used and deactivated 0.4% Pt/Al_2O_3 reforming catalyst by treating it in air at 480°C. In their case, the dispersion almost doubled from 0.37 to 0.72 after treatment. But treatment in oxygen or air at temperatures above 600°C

resulted in heavy sintering of catalysts compared to the degree of sintering for similar treatment in hydrogen (12, 13, 14). Wynblatt and Gjostein (12) sintered Pt on α-alumina at 700°C in both air and oxygen. The degree of sintering increased as the oxygen content in the atmosphere increased.

In more recent studies by Flynn and Wanke (13) and Fiedorow and Wanke (14), the effect of metal loading, time and temperature on the rate of sintering of Pt on alumina was investigated. Their observations show that at 550°C in oxygen, redispersion was maximum and independent of treatment time, while at higher temperatures the dispersion decreased with treatment time. At lower temperatures the degree of redispersion was less. The amount of redispersion decreased as the metal loading increased from 1% to 4% Pt by weight.

Bett *et al.* (15, 16, 17) investigated the characteristics of Pt/carbon catalysts in detail. They found the effect of treating Pt/carbon catalysts in hydrogen, nitrogen and in liquid acidic environment. No increase in activity was observed in any experiment, and samples sintered heavily in liquid phosphoric acid at considerably lower temperatures than in hydrogen and nitrogen. The catalyst was found to be most stable in nitrogen. Only small amounts of methanation of carbon support was observed at temperatures as high as 600°C in the presence of hydrogen. They measured chemisorbed hydrogen by an electrochemical method to get dispersion of the metal after each treatment step. This technique is described in detail in ref. (15). They consider this method to be superior over standard gas-phase chemisorption measurement techniques for Pt/carbon catalysts.

Hassan *et al.* (18) have reported results contradictory to most of the other workers on sintering of Pt/alumina in temperature range of 300 to 800°C in nitrogen, hydrogen, oxygen and in vacuo, in a recently published work. In this work they report that treatment of 1% Pt on alumina in nitrogen, hydrogen and in vacuo leads to an increase in activity at temperatures above 400°C, while in oxygen, activity decreases as the temperature is increased beyond 300°C and no reactivation was observed. They measured the activity of the catalyst by two model reactions, hydrogenation of cyclohexane and decomposition of hydrogen peroxide. This is the only published work so far which claims reactivation of catalyst due to treatment in nitrogen and hydrogen and no reactivation of catalyst in oxygen in the temperature range of 400 - 600°C.

There are only a few citations in the literature reporting sintering behaviour of supported metals other than platinum. Hughes *et al.* (19) studied the sintering behaviour of 0.3% Rh and 3% Ni on alumina in nitrogen at 900°C for 72 hours. The reduction in the activity of rhodium was about 60% compared to 90% for nickel. Wanke and Dougharty (20, 21) reported thermal stability of 5% Rh on η-alumina in oxygen at 600, 700 and 800°C. Yates and Sinfelt (22) also reported sintering of 5% Rh on silica in air at 538°C and 800°C for 4 hours, but rhodium was not in elemental form on the support surface prior to sintering. No significant redispersion for rhodium was observed in any of the studies.

According to a study by Aben (23), palladium is a thermally more stable catalyst when supported on silica compared to alumina. A limited amount of data is available on sintering behaviour of nickel supported on alumina, alumina-silica and silica (24, 25, 26), other than

previously mentioned. Armstrong *et al.*(27) have reported some data on changes in catalytic activity of supported Pt, Ir and other mixtures of noble metals in steam at 1000°C to 1200°C. It was found that for supported Pt-Rh and Pt-Ru, steaming at 1000°C results in increases in activity.

The use of supported metal catalysts in emission control devices in automobiles warrants further investigations on thermal deactivation of these catalysts under the severe conditions encountered in automobile catalytic converters. The literature contains very little information on loss of metal dispersion under these conditions.

2.2.2 Correlations

Most of the data presented in literature have been discussed qualitatively. Herrmann *et al.*(1) and Maat and Moscou (2) fitted their sintering data to a second order rate equation as mentioned previously. However, the majority of data can be correlated in a similar fashion by a power law function of the form

$$-\frac{dS}{dt} = k\, S^n \qquad (2.1)$$

where S is the metal surface area and the rate constant, k is assumed to obey Arrhenius law, *i.e.*

$$k = A\, e^{-E/RT} \qquad (2.2)$$

The value of n was found to vary anywhere from 2 to 14 for different investigations. Generally speaking, a large value of n fitted the equation for oxygen containing atmospheres; while sintering rate in nitrogen and hydrogen environments are fitted with lower values of n, except for the temperature range of 400 to 600°C, where for oxygen

negative values of n would be required if this equation was used to describe redispersion.

In few cases, dispersion as a function of time was found to be described by the equation

$$D = a\, t^{b} \qquad (2.3)$$

where values of a and b change with temperature for a particular catalyst.

In their review paper, Wanke and Flynn (28) have determined activation energy, E, and power law order, n, for many cases. They have also presented an exhaustive review of the literature and have given a detailed summary of most of the data reported on sintering.

2.3 Mechanistic Models

Two mathematical models have been advanced recently to describe the mechanism of sintering of supported metal catalysts. The first model postulates that metal crystallite growth takes place by the movement of metal crystallites on the support surface followed by their collision and fusion with other crystallites, resulting in increase in the size of metal particles and hence loss in metal surface area. This model, developed by Ruckenstein and Pulvermacher (29, 30), is referred as crystallite migration model. A second model, proposed by Flynn and Wanke (31, 32), postulates that sintering occurs by a three step mechanism, loss of atoms from metal crystallites, transportation of these species on the support surface and their incorporation into stationary metal crystallites upon collision. This model will be referred as the atomic migration model. A detailed description of these models is beyond the scope of this work, but a short qualitative

summary of both is presented below.

2.3.1 Crystallite Migration Model

This model envisages metal crystallites to move along the surface of the support as separate entities, and to merge with other crystallites upon collision. When two crystallites collide, two limiting situations can occur; first, the interaction between the colliding particles is very strong so that they form a single unit within a time which is short compared to the diffusional time; and second, when the time of merging process of the colliding particles into a single unit is long compared to the diffusional time. The second situation occurs when support-metal interactions are strong compared to metal-metal interactions. For the first situation, the rate of sintering is diffusion controlled and in the second situation, the merging of two crystallites is a rate determining step. The latter case is called 'sintering control'.

Ruckenstein and Pulvermacher used equation 2.1 to describe the rate of sintering. They concluded that n varies from 4 to 8 for diffusion controlled decay and it is less than 3 for sintering controlled decay. They also postulated from this model that rate of sintering is independent of initial particle size distribution.

To account for redispersion, Ruckenstein and Pulvermacher proposed that due to changes in interfacial energies, (which are a function of the atmosphere to which catalyst is exposed during treatment), the crystallites split into smaller crystallites. At temperatures of redispersion, splitting of crystallites occur faster than migration-collision-coalescence and at higher temperatures, this trend is reversed to account for observed rapid decrease in dispersion.

There are few cases reported in the literature where crystallite splitting has been reported of Pt on alumina films (12, 33). But the conditions encountered in these experiments are drastically different than conditions under which redispersion of Pt have been observed.

Some recently published results contradict the crystallite migration model. Baker *et al.*(34) carried out *in situ* studies of particle growth of Pt on alumina in oxygen and nitrogen atmospheres up to a temperature of 920°C, in an transmission electron microscope with the help of a movie camera. They found that in all their experiments, the platinum particles once formed remained immobile on the support surface throughout the heating cycle, indicating that particle growth occurred via the movement of particles less than 2.5 nm in size. Furthermore, Wynblatt and Gjostein (35) showed on the basis of theoretical predictions that the merging of metal crystallites (step 2) cannot control the rate of sintering at temperatures above 500°C, which means that sintering control case is generally not feasible under normal sintering conditions. There is other experimental evidence to show that this mechanism cannot be the exclusive mechanism for sintering and some other mechanism is also responsible for observed particle growth of metal crystallites.

2.3.2. Atomic Migration Model

The mechanism of sintering of supported metal catalysts in this model is postulated to consist of three steps: one, individual metal atoms or molecules (such as PtO, when the catalyst is sintered in oxygen), move from the metal particles to the support surface; two, migration of atomic species along the surface of support; and three, capture of metal atoms by collision with a metal crystallite. The third

step could also be replaced by immobilization of metal atoms by a sudden drop in temperature or encountering an energy well on the support surface.

This model envisages that forces other than van der Waals are important in increasing metal-support interaction, so that loss of atoms from metal crystallites is substantial at sintering temperatures. The factors which increase metal-support interactions include presence of defects and impurities on support surface. The presence of oxygen significantly increases the interaction of metal crystallites and oxide supports which is believed to be caused by formation of a metal oxide at support surface. Flynn and Wanke (31) proposed that the rate of loss of atoms from a metal crystallite, i, can be described as

$$\frac{dL_i}{dt} = A \; e^{-E_a/RT} \qquad (2.4)$$

where $\frac{dL_i}{dt}$ is the rate of transfer of atoms to the surface, A is a constant and E_2 is the activation energy required to move an atom from a crystallite to the support surface.

Once the atoms are on the surface, they may be considered as a two dimensional gas and move quite freely. Their motion can be described by kinetic theory of gases or by jumping from one surface site to the next. Their movement on the surface is assumed to be rapid enough at sintering temperatures, so that there is a uniform concentration of free surface metal atoms on the support surface.

The rate at which a crystallite gains metal atoms by collision depends on the concentration of metal atoms on the support surface, velocity of these atoms, v, and the effective capture diameter of the crystallite, D_i, or

$$\frac{dG_i}{dt} = \alpha \frac{v}{N_t} \frac{F_s}{S_o} D_i \qquad (2.5)$$

where α is sticking probability of an atom colliding with crystallite, N_t is total number of metal atoms, S_o is support area per metal atom and F_s is number of atoms migrating on support with an area $N_t S_o$. $F_s/N_t S_o$ represents the concentration of metal atoms on the support surface.

The net rate of change of number of atoms in a given crystallite i is then

$$\frac{dN_i}{dt} = \frac{dG_i}{dt} - \frac{dL_i}{dt} \qquad (2.6)$$

Because smaller crystallites tend to equilibrate with higher concentrations of migrating surface atoms than larger crystallites (Kelvin equation), the larger crystallites grow while smaller ones decay. Flynn and Wanke solved equation 2.6 for two cases: one, when rate of capture of migrating surface metal atoms is large, (or when α/S_o is large), resulting in negligibly small concentration of surface atoms; and two, when the rate of capture of metal atoms is low (or when α/S_o is small), resulting in appreciable concentration of surface atoms. The first situation occurs when support-metal interactions are weak or metal loading is high (S_o is small) and second situation occurs when support-metal interactions are strong or metal loading is low.

The model predicts a strong dependence of the rate of sintering on initial metal partical size distribution (PSD). For broad PSD, the catalyst is predicted to sinter rapidly compared to narrow PSD. The model also predicts an initial increase in dispersion because of build-up of metal atoms on the support surface.

These atoms can be immobilized on support surface by quenching the catalyst at this stage, resulting in net increase in dispersion. As mentioned previously, the support-metal interactions are influenced by the type of atmosphere. This influences the ease with which metal atoms can escape from crystallites. Large metal-support interactions lead to a higher concentration of surface metal atoms. Therefore, oxygen, which decreases the energy barrier between metal atoms in crystallites and on the surface by forming metal oxides, causes substantial initial increase in dispersion.

This model has been able to explain many of the observations of sintering studies satisfactorily. But it has a noticeable theoretical limitation. Even at temperatures as high as 800°C, metal-support interactions are barely able to surpass the energy barrier required for escape of metal atoms from crystallites. Also, the initial PSD has to be known to predict the rate of sintering by the atomic migration model and often it is very difficult to get a reliable measure of initial PSD.

A third model, which postulates that metal transport occurs by evaporation and condensation of metal atoms, has very serious limitation of explaining sintering at temperatures where partial pressure of metals are very small; and hence its contribution to the sintering of supported metal catalysts is negligible.

On the basis of available experimental data, it is difficult to discriminate conclusively between the crystallite migration and atomic migration models. In the present investigation, the effects of types of metal and types of support on the sintering behavior were studied. The results will be examined in terms of the two sintering mechanisms.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Introduction

This chapter describes the procedures used in this work for the preparation and treatment of catalysts. A short description of the method and apparatus employed for dispersion measurement, as well as the BET apparatus and x-ray diffractometer used for support area and crystal structure measurements, is also presented. Details of the surface area determinations and x-ray diffraction studies are given in Appendices A and B.

3.2 Catalyst Preparation and Treatment Procedure

3.2.1 Catalyst Preparation and Pretreatment

Both commercial and laboratory prepared catalysts were used in this work. The commercial catalysts were purchased from Englehard Industries, and were reduced in batches (~ 25 g each) before using in sintering experiments. Since these catalysts had been calcined at an elevated temperature by the manufacturer, a thorough reduction, consisting of treatment at 250°C for 1 hour and 500°C for 16 hours in flowing hydrogen (50 cc(STP)/min), was carried out. After the reduction at 500°C, the catalyst batch was degassed in flowing helium at 500°C for 1 hour and cooled to room temperature in flowing helium. The catalyst batches were then stored in air at room temperature until use.

The laboratory prepared catalysts were made by impregnation of supports with aqueous solutions of various metal salts followed by drying and reduction. The impregnation technique used consisted of completely wetting the support with distilled water, adding the desired

amount of metal salt solution to the wetted support, briefly stirring the support-solution mixture vigorously and then stirring the support-solution mixture intermittently over the next 24 hour period. The catalyst was then dried at 110°C in a Fisher Isotemp oven for 24 hours. The reduction of the dried catalyst consisted of four steps: one, the catalyst was reduced in flowing hydrogen (50 cc/min) at 150°C for 16 hours; two, the temperature of furnace increased to 250°C in approximately 10 minutes and kept for another 2 hours at this temperature; three, the temperature was raised to 500°C in about half an hour and reduction continued for one more hour at 500°C (hydrogen flow maintained during steps 2 and 3); and four, the hydrogen was replaced by helium and the catalyst was degassed for one hour at 500°C. At the end of this procedure the catalyst was removed from the furnace and cooled to room temperature in helium. The catalysts were stored until use at room temperature in air after reduction.

3.2.2 Sintering Treatment

A portion of the reduced catalyst, to be used for a sintering experiment, was placed into a Vycor U-tube. A fresh sample was used for sintering at each temperature in a particular atmosphere, but the same sample was used for sintering at different lengths of time. Except for a few cases, the treatment cycle followed this pattern: the sample was treated for one hour and its dispersion was measured; it was sintered for another 3 hours and again its dispersion was measured; and finally it was treated for 12 hours more before final measurement of its dispersion. The samples thus treated were considered to be sintered for 1, 4 (1+3) and 16 (1+3+12) hours, respectively. An approximately constant amount of catalyst was used for each kind of catalyst. The

amount of samples used for individual runs, along with type of catalyst, are shown in tables B-1 and B-2 in Appendix B.

The following standard treatment procedure was adopted for all sintering experiments:

1. The furnace was heated to the desired treatment temperature.
2. The U-tube containing the sample was first flushed with nitrogen or helium in case of treatment in oxygen. After 5 minutes of flushing oxygen flow was started at room temperature at a rate of 50 cc(STP)/min. In case of treatment in hydrogen, flushing with inert gas was omitted and hydrogen flow was started at room temperature.
3. The Vycor tube containing the sample was inserted into the furnace and left for the desired treatment time. The treatment time was measured from the time that the furnace regained the set-point temperature. This took about two minutes after the insertion of the sample.
4. In case of treatment in oxygen, the oxygen flow was replaced by nitrogen or helium at the end of treatment time, the sample tube was removed from the furnace and cooled to room temperature in flowing inert gas. For sintering in hydrogen, the sample was cooled to room temperature in flowing hydrogen.

For all treatments (including reduction and pretreatment steps), a modified Thermolyne muffled furnace was used. The furnace temperature was controlled to the accuracy of $\pm$ 2°C with the help of a J-type iron-constantan thermocouple and Thermo-Electric 400 type temperature controller.

3.3 Dynamic Adsorption Method

The metal dispersion of the catalyst samples was determined by measuring the amount of hydrogen chemisorbed by catalyst sample. The pulse dynamic adsorption method was used to measure chemisorbed hydrogen. Dispersion was calculated assuming a 1:1 stoichiometry between adsorbed H atoms and metal surface atoms. The calculation procedure is detailed in Appendix A.

All catalyst samples were pretreated with the same procedure before carrying out the hydrogen chemisorption measurements to ensure that the catalyst surface is in the same condition prior to measurement for all runs. Pretreatment consisted of two steps: one, the catalyst was reduced in flowing hydrogen (50 cc/min) at 500°C for one hour; and two, the sample was degassed for two hours in flowing nitrogen (50 cc/min) at 500°C and then cooled to room temperature in flowing nitrogen. The chemisorption measurement was carried out immediately after pretreatment.

Hydrogen pulses (18.7 μmoles of hydrogen per pulse) were injected into the nitrogen carrier stream at 3 minute intervals. The flow rate of nitrogen carrier gas was kept constant at 45 cc(STP)/min for all adsorption measurements. A two loop electrically actuated Carle gas sample valve (Model 4200) was used to inject the hydrogen pulses. The amount of hydrogen not adsorbed by the catalyst sample was measured by a thermal conductivity cell (manufactured by Gow-Mac Instrument Co., model #10-735). The T.C. cell was kept in an ice-water mixture and connected to a Varian A-25 recorder-integrator, which recorded the amount of hydrogen passing through the T.C. cell in the form of peaks. The pulses were injected until the height of

two consecutive peaks was the same to ensure that no more hydrogen was being adsorbed by the catalyst. The amount of hydrogen adsorbed was calculated as the difference between the amount of hydrogen injected and the amount of hydrogen eluted.

A schematic diagram of the apparatus is shown in Figure 3.1. A complete description of the apparatus including procedure for calibration of sample valve has already been given by Flynn (36) and hence is not included here. It should be pointed out that the sintering, reduction and adsorption procedures were carried out without removing the catalyst sample from the sample U-tube.

The gases used for all experiments were of high purity grade to avoid contamination of catalyst surface. Hydrogen was generated in the laboratory by a Matheson 8320 (Elhygen-R) hydrogen generator and was purified by passing it through an Englehard Deoxo hydrogen purifier and molecular sieve bed before entering the rotameter.

Prepurified grade nitrogen supplied by Linde was used after passing it over Cu/Cu_2O and molecular sieve beds to remove traces of hydrogen, oxygen and water. Oxygen and helium used were both of ultra high purity grade, were supplied by Linde and were used without any further purification.

3.4 X-Ray Diffractometer

A Phillips (type PW 1380/60 no. 0698) X-ray diffractometer was used to determine the crystalline structure of the support. These experiments were conducted to determine the effect of thermal treatment on the support crystalline structure. The X-ray diffraction patterns were measured for the fresh and heavily sintered samples. Cu-K α radiation was used (copper tube with a nickel filter). The scanning

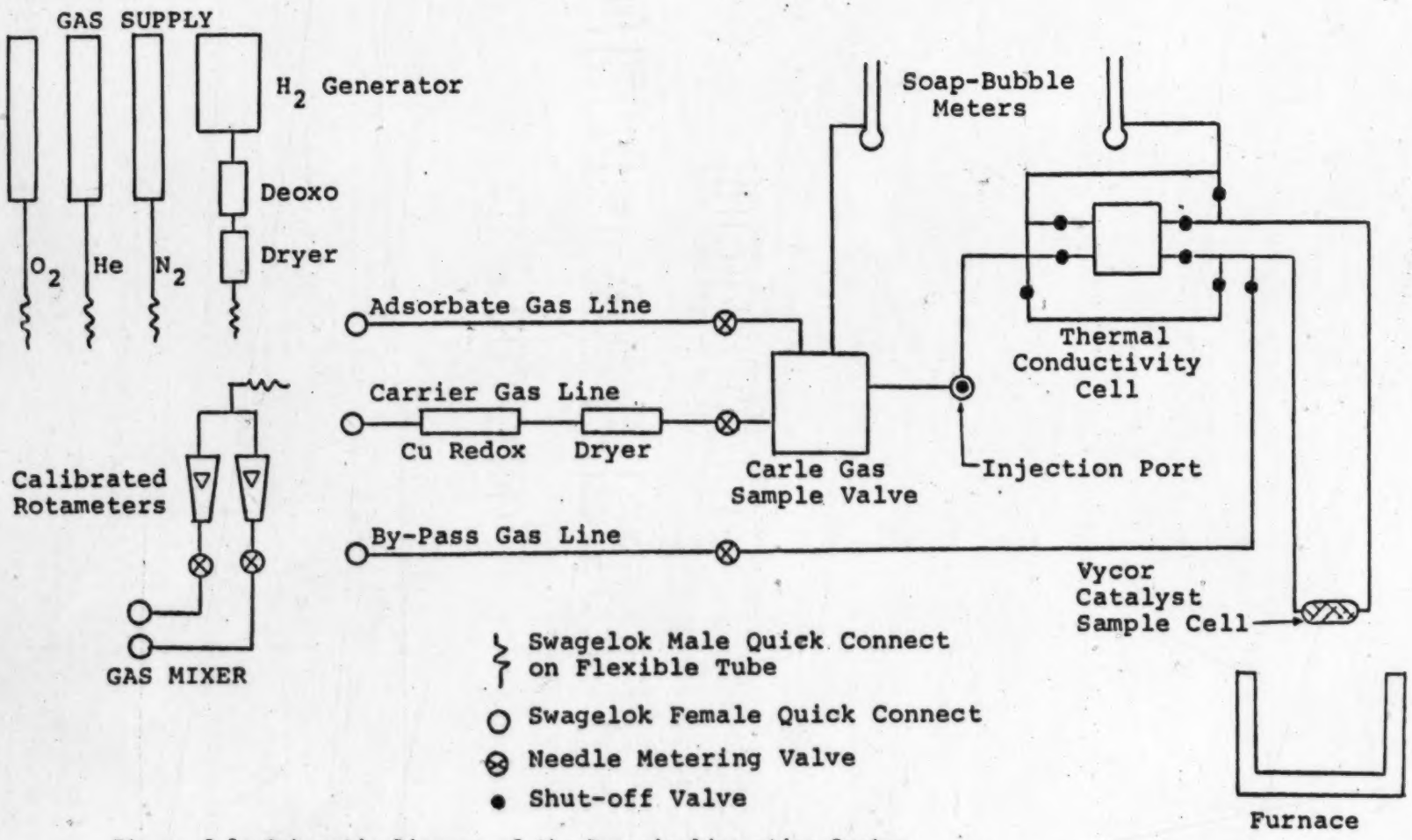

Figure 3.1: Schematic Diagram of the Dynamic Adsorption System

rate was 0.25° per minute.

3.5 BET Apparatus

Surface areas of the supports were measured by using a standard constant volume BET apparatus. The dead volume determinations were done using helium and the BET isotherms were measured using nitrogen at liquid nitrogen temperatures. The vapor pressure of nitrogen at the liquid nitrogen temperatures was measured with a Wallace-Tiernan pressure gauge. The pretreatment of catalyst consisted of evacuating the samples at 200°C to a pressure of $\leq 10^{-3}$ Torr. An average of 5 points in the range of $0.05 \leq P/P_o \leq 0.35$ were measured for each surface area determination. Again the surface areas of support were measured for fresh and heavily sintered samples only, to determine the changes of support area during sintering.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

Two series of experiments were conducted to explore the sintering behavior of supported metal catalysts. In the first series of experiments, the sintering behavior of platinum, rhodium and iridium supported on alumina was investigated. The sintering behavior of supported platinum on γ-alumina, silica-alumina, and silica gel was studied in the second series of experiments. The BET isotherms and X-ray diffraction patterns were measured for catalysts used in both series of experiments. The results from both the series of experiments are reported in section 4.2 followed by discussion of these results in Section 4.3.

4.2 Results

The catalysts used in this study are described in Table 4.1. The metal content of the catalysts prepared by impregnation were calculated from the weight of the support and the amount of metal in the impregnating solutions. The impregnation technique resulted in an uneven distribution of the metal in the support pellets; the metal concentration decreased towards the interior of the pellets. Some fines ($\leq$ 5% by weight of the support used) were formed due to stirring during the impregnation procedure. The colour of these fines indicated that they probably had, on the average, a higher metal content than the impregnated support spheres. Hence, the nominal metal content reported in Table 4.1 may be somewhat higher than the actual metal content.

In order to calculate the metal dispersions (the ratio of

TABLE 4.1

DESCRIPTION OF CATALYSTS

Catalyst	Catalyst Composition	Method of Preparation	Initial Dispersion (D_o)	Sample Size Used for Sintering(g)
1	0.5% Rh on alumina	Commercial Catalyst (Englehard; Lot 17-941)	0.42 (±11%)	3.0
2	1.0% Rh on Kaiser KA-201 alumina	Impregnation with $RhCl_3$ solution	0.32	3.0
3	2.0% Pt on Kaiser KA-201 alumina	Impregnation with H_2PtCl_6 solution	0.28 (±10%)	2.5
3A*	2.0% Pt on Kaiser KA-201 alumina	Impregnation with H_2PtCl_6 solution	0.35 (±9%)	2.5
4	0.5% Pt on alumina	Commercial Catalyst Englehard; Lots 18-381 and 23-288)	0.20 (±9%)	5.0
5	2.0% Ir on Kaiser KA-201 alumina	Impregnation with $IrCl_3$ solution	0.42	5.0
6	1.0% Pt on granular silica gel (Alfa Products)	Impregnation with H_2PtCl_6 solution	0.13 (±15%)	3.0 and 5.0
7	1.0% Pt on silica-alumina (Alfa Products)	Impregnation with H_2PtCl_6 solution	0.17 (±22%)	5.0
8	1.0% Pt on γ-alumina (Alfa Products)	Impregnation with H_2PtCl_6 solution	0.27 (±15%)	5.0

*This catalyst is the same as '3', but was prepared in a separate batch.

surface to total metal atoms) from hydrogen adsorption uptakes, one has to know the adsorption stoichiometry, *i.e.* the number of hydrogen atoms adsorbed per surface metal atom. For supported Pt, and to a lesser degree for supported Rh, considerable evidence exists that one hydrogen atom adsorbs per surface metal atom. Very little information is known about the stoichiometry of hydrogen for supported Ir. The dispersions listed in Table B-2 were calculated using the assumption that one hydrogen atom adsorbs per surface metal atom.

In the present study we are interested in the relative stability of various supported metal catalysts. The dispersions, D, determined by hydrogen adsorption after various treatments were normalized with respect to the dispersions for the fresh catalysts, D_0. This normalized dispersion, D/D_0, is then a measure of the change in dispersion due to the thermal treatment. Furthermore, the value of D/D_0 is independent of the hydrogen adsorption stoichiometry as long as this stoichiometry is not a function of the thermal treatment. It is for this reason that the results in the subsequent sections are presented in terms of D/D_0.

4.2.1 Reproducibility of Dispersion Measurements

A measure of the reproducibility of hydrogen adsorption uptakes, from which the dispersion was calculated, is the coefficient of variation (40), CV, for runs where repeat adsorptions were carried out. Repeat adosprtions were carried out for 222 runs of the runs listed in Table B-2. The average value of the CV for these 222 runs was 7.4%. For 52 of the runs CV was >10%. Examination of data shows that for 40 of the 52 runs the total amount of hydrogen adsorbed was < 20 μmole (< 1 pulse).

A total of 87 runs resulted in hydrogen uptakes of < 20 μmoles, *i.e.* 39% of the total runs were responsible for 77% of the runs with CV >10%. The average value of CV for 135 runs with hydrogen uptakes >20 μmoles was 4.3%. This dependency of the reproducibility on the amount of hydrogen uptake is not unexpected since reliability of measuring the amount of hydrogen adsorption is of the order of ± 2 μmoles (± 0.1 pulse). This error is due to equipment limitations (*e.g.* slight pressure fluctuations, alignment of sample ports in pulse injection valve and integration of areas under eluting peaks) and irreproducibilities in procedure (*e.g.* slightly different reducing and degassing times and temperatures, derivations in times between pulse injections, and variations in adsorption temperature). The reproducibility in the dispersions calculated from the hydrogen adsorption uptakes is more than adequate for the determination of relative stabilities.

Repeat adsorptions were carried out on a number of catalysts that had been stored in air for periods of up to several months after thermal treatment. The results of these experiments are summarized in Table 4.2. The standard adsorption pretreatment (reduction and degassing) was done before the repeat adsorptions.

The results for Catalyst 1 (0.5% Rh/Al_2O_3) do not show any unusual behavior, *i.e.* the repeat dispersions are essentially equivalent to the dispersions measured immediately after the treatment. The 2% Pt/Al_2O_3 (Catalyst 3), on the other hand, shows some unexpected behavior. The dispersions measured after treatment in oxygen and exposure to air are considerably lower than the dispersions measured immediately after the oxygen treatment at < 700°C. After oxygen treatment at ≥ 700°C, the exposure to air does not appear to influence

TABLE 4.2

Results of Repeated Hydrogen Adsorption After Sintered Catalysts Were Exposed to Air

Cat.	Treatment Atm.	Temp. (°C)	Time (h)	Dispersions After Treatment	Repeat After Exposure to Air	Runs
1	O_2	550	1	0.381	0.355	ERH 46 & ERH 46 1
		700	1	0.298	0.302	ERH 50 & ERH 50 1
	H_2	550	1	0.372	0.401	ERH 47 & ERH 47 1
		700	1	0.357	0.341	ERH 51 & ERH 51 1
		800	1	0.267	0.281	ERH 56 & ERH 56 1
3	O_2	500	1	0.680	0.458	19 & PT 19 1
		550	1	0.652	0.467	3 & 3R,3R/2
		600	1	0.652	0.590	20 & PT 20 1
		700	16	0.112	0.106	7 & 7R
		800	1	0.039	0.047	C & PT C 1
	H_2	600	1	0.234	0.329	D & PT D 1
		700	1	0.193	0.284	18H & PT 18H 1
		800	1	0.110	0.180	B & PT AB 1
5	O_2	300	1	0.439	0.406	IR 98 & IR 98 1
		400	1	0.489	0.424	IR 107 & IR 107 1
		500	1	0.322	0.259	IR 87 & IR 87 1
		700	1	0.055	0.052	IR 89 & IR 89 1
	H_2	600	1	0.381	0.368	IR 86 & IR 86 1
		700	1	0.358	0.354	IR 76 & IR 76 1
		800	1	0.341	0.339	IR 63 & IR 63 1

subsequent dispersion measurements. Exposure to air of Catalyst 3 after hydrogen treatment increases the dispersion. The behavior of the Ir catalyst after treatment in oxygen is similar to that of the Pt catalyst although the effect is less marked. Treatment in hydrogen followed by exposure to air does not appear to effect the Ir dispersion.

At present, the author has no explanation for these observations. These results are presented here to illustrate some of uncertainties in the results and to give future investigators food for thought.

Another factor to be considered is homogeneity of different catalyst samples taken from the same batch of catalysts. Table 4.1 lists the percent standard deviation in the determination of the initial dispersion for the various catalysts. As can be seen from these results the average variation is considerably larger than the variations in hydrogen adsorption uptakes. Therefore it is concluded that the variations in D_o are due to variations in metal content from pellet to pellet. Differences in the color of the pellets indicating differences in composition in the same batch were apparent. These variations in composition (and possibly metal crystallite size distributions) among samples of the same catalyst is one of the limiting factors in this work.

4.2.2 Different Metals Supported on Alumina

4.2.2(a) Supported Platinum

The sintering behavior of 2.0% Pt on Kaiser alumina and 0.5% Pt commercial Englehard catalyst is shown in Figures 4.1 and 4.2. The normalized dispersions as a function of sintering atmosphere, time and temperature are shown in these figures. Two batches of 2.0% Pt on Kaiser

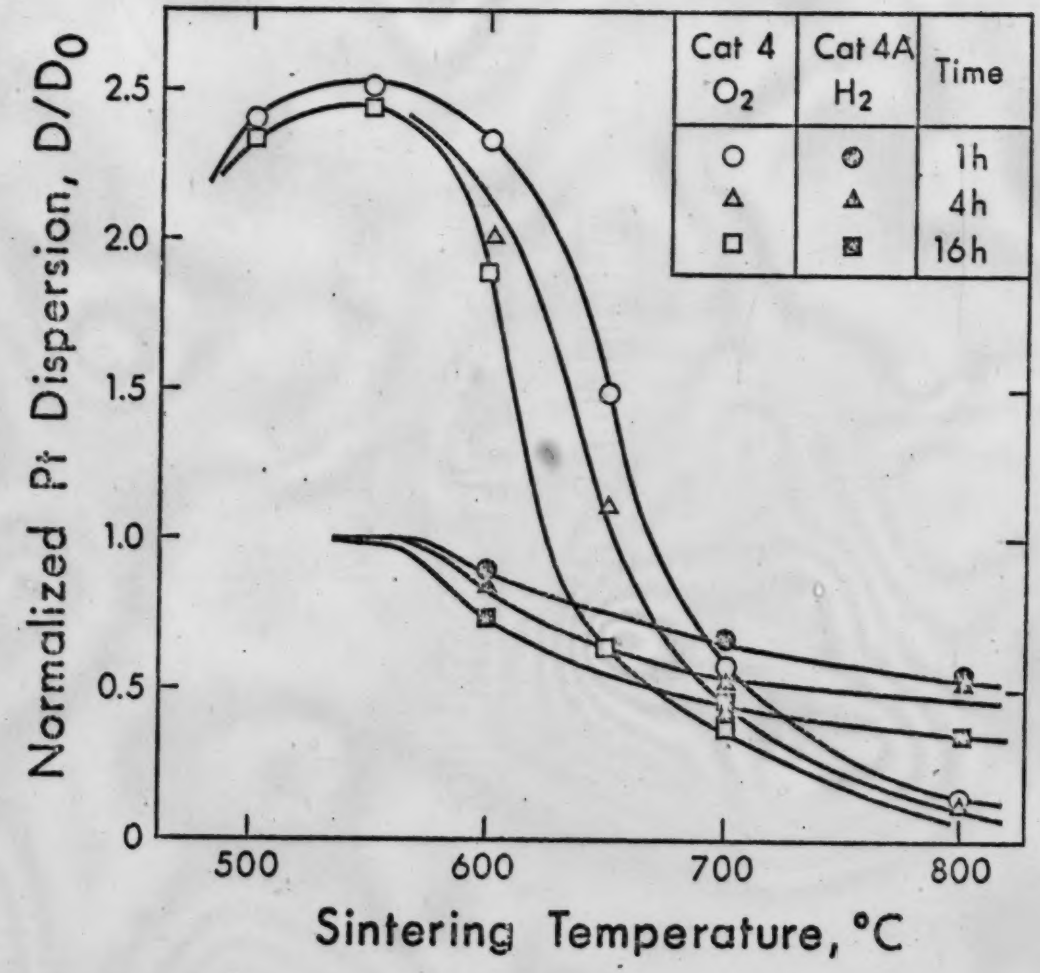

Figure 4.1: Effect of Treatment in Oxygen and Hydrogen on the Normalized Dispersion of 2.0% Pt/Al_2O_3.

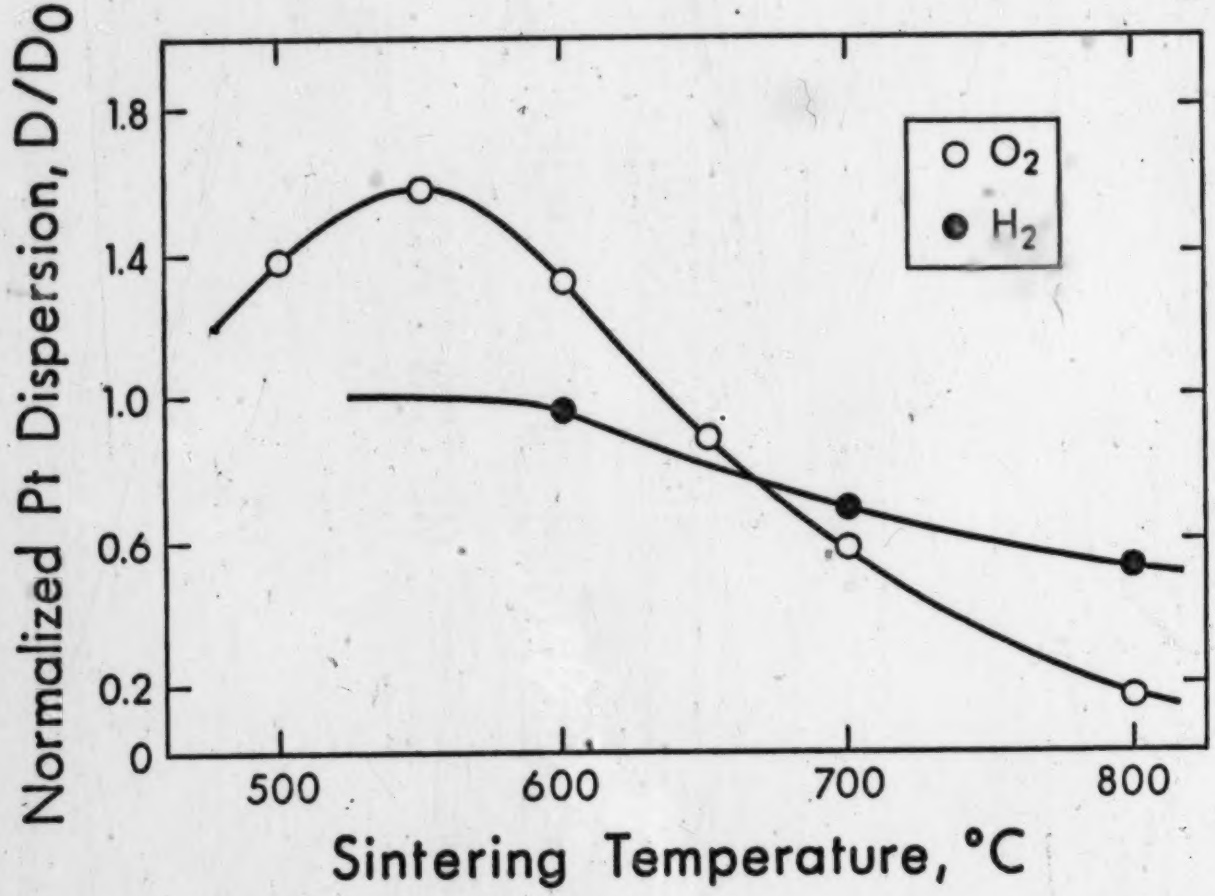

Figure 4.2: Effect of treatment in oxygen and hydrogen for 1 h on the normalized dispersion for 0.5% Pt/Al_2O_3.

KA-201 alumina were prepared. For the first batch, the initial dispersion was 0.28 and for the second batch it was 0.35. The preparation method was the same for both batches. The initial dispersion was 0.20 for Englehard catalyst (0.5% Pt on alumina).

The disperions after treatment in oxygen at $\leq$ 600°C were higher than the initial dispersion for both laboratory prepared and commercial catalyst. The maximum dispersion varied from 1.5 to 2.5 times the initial dispersion. It occured after treatment at 550°C for both catalysts. In Figure 4.1, the effect of length of treatment is also shown. For temperatures $\leq$ 550°C the dispersion is independent of length of treatment time, while at higher temperatures, the dispersions for 16 hour treatments are significantly lower than 1 hour treatments.

The treatment in hydrogen resulted in monotonic decreases in the metal surface area with increasing sintering temperature. Increasing the sintering time also resulted in decreased values of the dispersion. Sintering in hydrogen never resulted in increased Pt dispersions.

4.2.2(b) Supported Iridium

Sintering behavior of a 2.0% Ir on Kaiser KA-201 alumina was studied. The average initial dispersion of the catalyst was 0.42. The results presented in Figure 4.3 show that supported Ir is considerably more stable in hydrogen than in oxygen atmosphere. Treatment in hydrogen for 16 hours at 800°C resulted in a 20% decrease in dispersion. Treatment in oxygen at 300°C resulted in small increases in Ir dispersion ($\sim$ 5%) for treatment times to 1 to 16 hours. Treatment at 400°C in oxygen for 1 hour resulted in an 18% increase in dispersion, but increasing the sintering time at 400°C to 4 and 16 hours resulted in

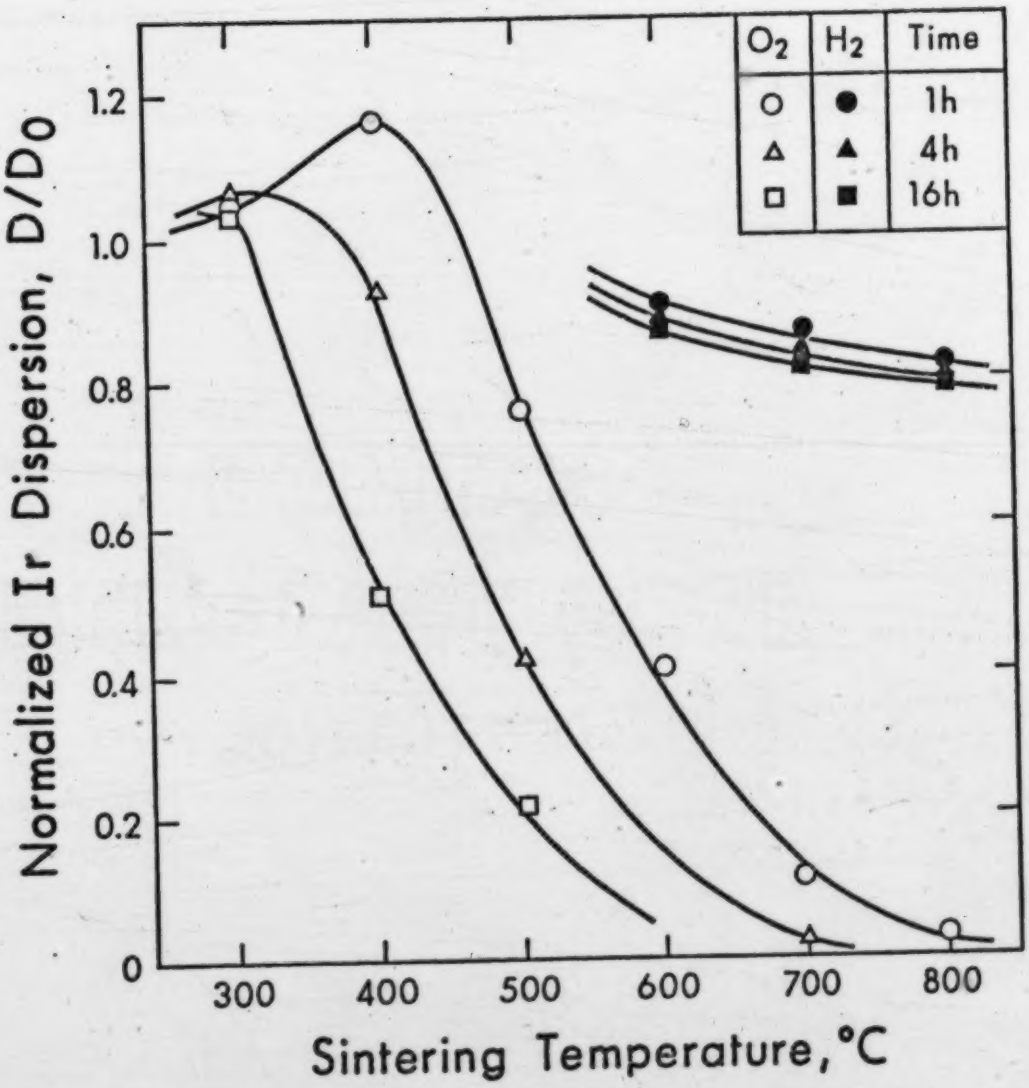

Figure 4.3: Effect of treatment in oxygen and hydrogen on the normalized dispersion for 2.0% Ir/Al_2O_3.

7 and 49% decreases in dispersion. Oxygen treatment at temperatures above 400°C resulted in rapid decrease in Ir dispersion. These results indicate that sintering of Ir in oxygen occurs by the same mechanism as that of Pt. These results are further discussed in a later section.

4.2.2(c) Supported Rhodium

Two rhodium catalysts were used in this study. The first catalyst used was commercial 0.5% Rh on alumina (Englehard) and the second one was 2.0% Rh on Kaiser KA-201 alumina. The second catalyst was prepared in the laboratory. The average initial dispersions for commercial and laboratory prepared catalyst were 0.42 and 0.32, respectively.

The normalized dispersion of these two Rh catalysts as a function of treatment temperature, time and atmosphere are presented in Figures 4.4 and 4.5. Treatment in oxygen did not result in any appreciable increases in dispersion. Sintering experiments in oxygen at 300 and 400°C resulted in a $D/D_0 \approx 1.0$. To determine whether treatment of sintered catalyst in oxygen at < 600°C results in increases in dispersion, a sintered sample of 0.5% Rh commercial catalyst (750°C in oxygen for 8 hours; $D/D_0 = 0.62$) was treated in oxygen at 500°C for 16 hours. After the 500°C treatment, the D/D_0 was found to be 0.59. A sintered sample of 1% Rh on Kaiser alumina (800°C in oxygen for 1 hour; $D/D_0 = 0.24$) was subsequently treated in oxygen at 500°C for 16 hours. D/D_0 after this treatment was 0.29, (results obtained by R. Fiedorow). These results show that treatment in oxygen at 500°C does not result in significant redispersion of Rh supported alumina.

Nevertheless, the presence of oxygen appears to have a retarding effect on the rate of metal surface area loss at temperatures

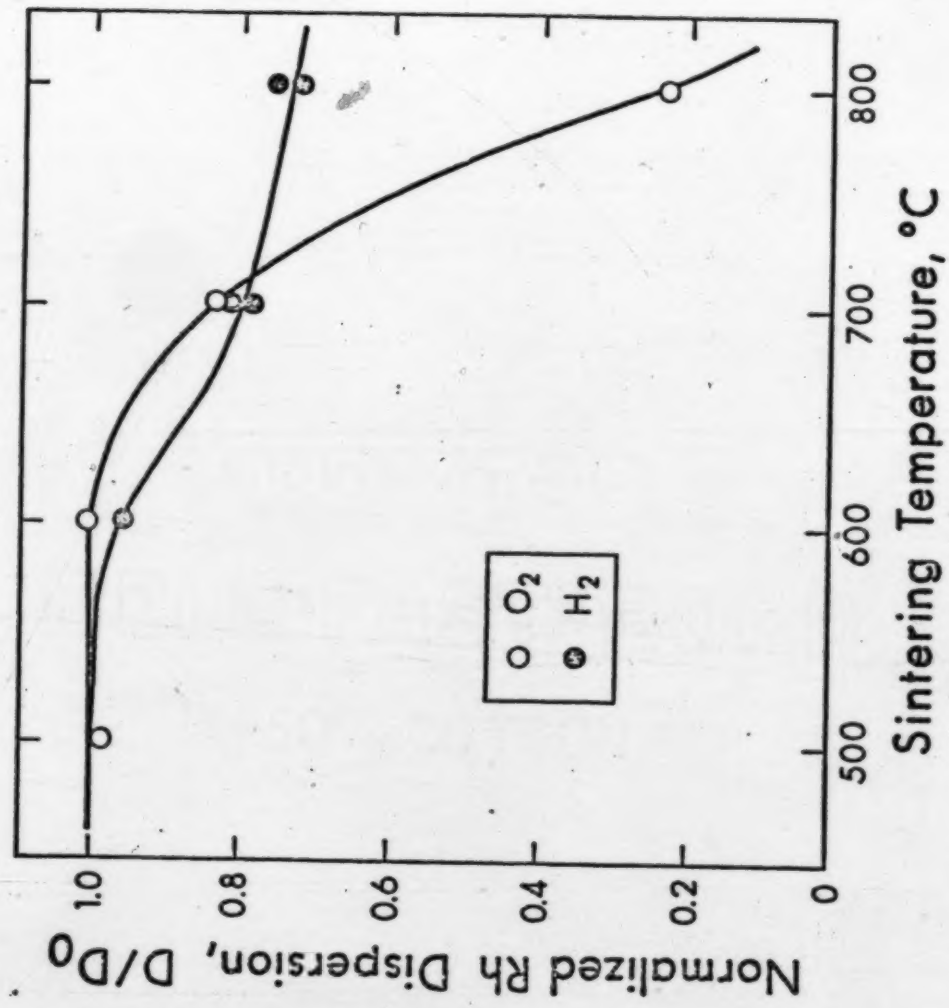

Figure 4.4: Effect of treatment in oxygen and hydrogen for 1 hour on the normalized dispersion of 1.0% Rh/Al_2O_3.

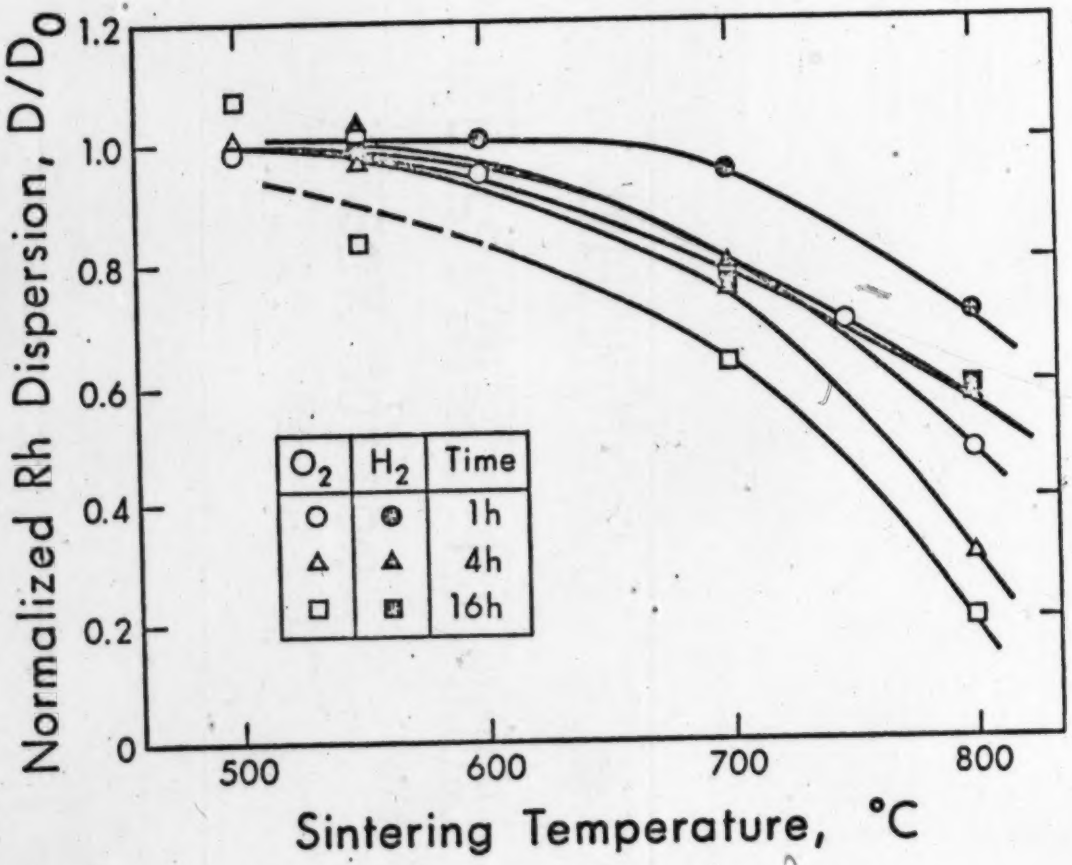

Figure 4.5: Effect of treatment in oxygen and hydrogen on the normalized dispersion of 0.5% Rh/Al_2O_3.

≤ 600°C. This is very noticeable when comparing the changes in dispersion for hydrogen and oxygen treatment of 1% Rh on Kaiser alumina (Figure 4.4). At temperature ≤ 700°C, the dispersion after treatment in oxygen is higher than the dispersion for similar treatment in hydrogen. This effect is less noticeable for commercial catalyst (Figure 4.5), but in this case the decrease of dispersion in oxygen at temperatures ≤ 700°C for oxygen treatment is higher than that for treatment in hydrogen, while at > 700°C the decrease in dispersion is about the same for both atmospheres (with the exception of the 1 hour treatment in hydrogen). Comparing the 1 hour sintering (Figures 4.4 and 4.5) shows that the 1% Rh/alumina is less stable than 0.5% Rh/alumina during treating in oxygen.

The situation is reversed for treatment in hydrogen, *i.e.* 1% Rh appears to have a greater thermal stability than 0.5% Rh. For the 1% Rh catalyst, the dispersion decreased significantly when the sintering temperature was increased from 600 to 700°C. Increasing the sintering temperature to 800°C resulted in a relatively small decrease in disperion. This was an unexpected observation, but repeat experiments with fresh catalyst samples resulted in excellent reproducibility (see Figure 4.4).

4.2.2(d) Effect of Thermal Treatment on Support Properties

The X-ray diffraction patterns of Kaiser KA-201 alumina and 2.0% Pt/Kaiser alumina samples (fresh and sintered) are shown in Figure 4.6. The X-ray diffraction patterns of fresh and sintered Ir/alumina and Rh/alumina samples are shown in Figures 4.7 and 4.8, respectively. These X-ray diffraction studies showed that no detectable change in the crystalline structure of the support occurred due to thermal

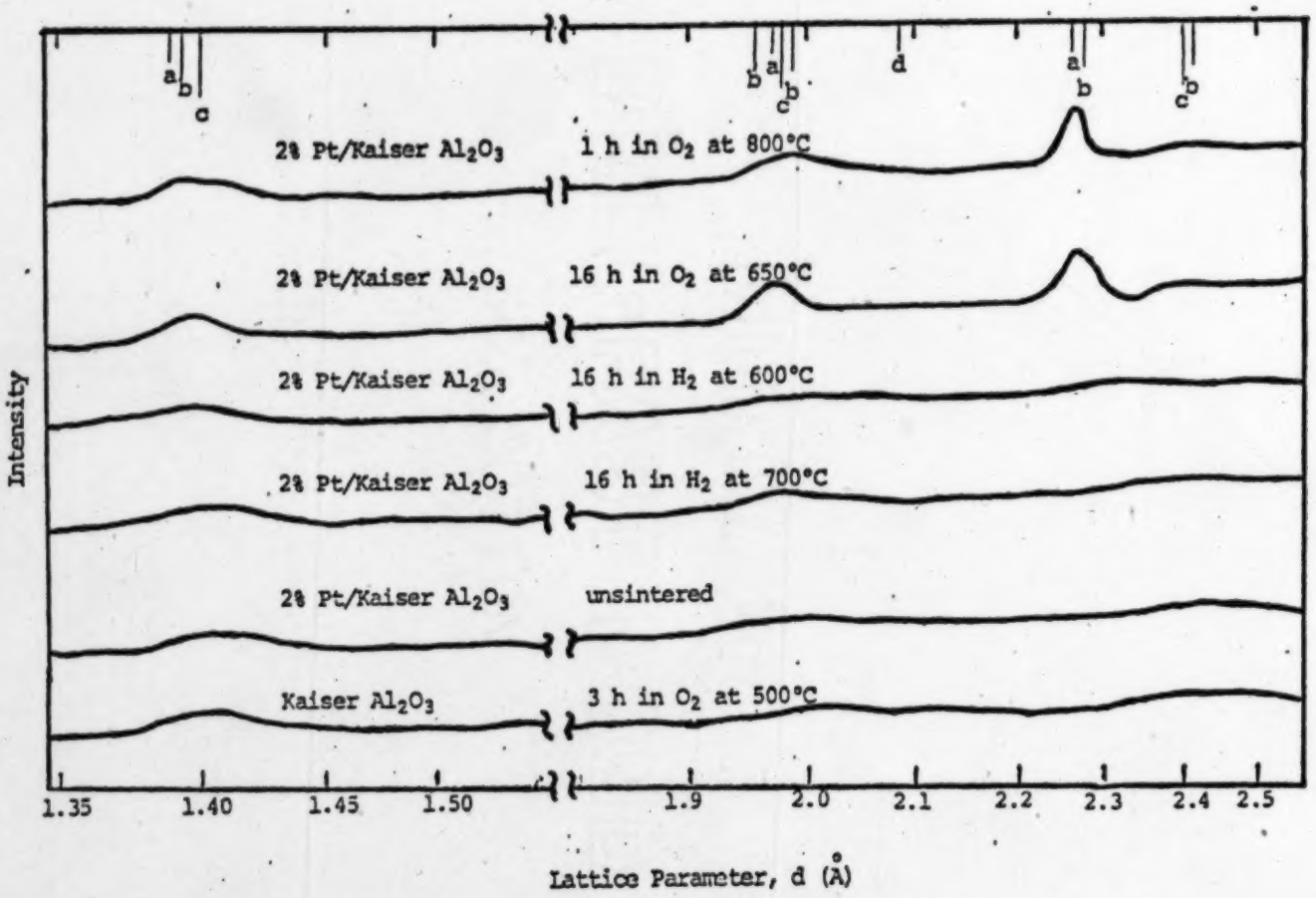

Figure 4.6: X-ray diffraction patterns of Kaiser KA-201 alumina and 2% Pt/Kaiser alumina after indicated treatments. (Lines indicated correspond to: a=Pt; b=γ-Al_2O_3; c=η-Al_2O_3 and d=α-Al_2O_3.)

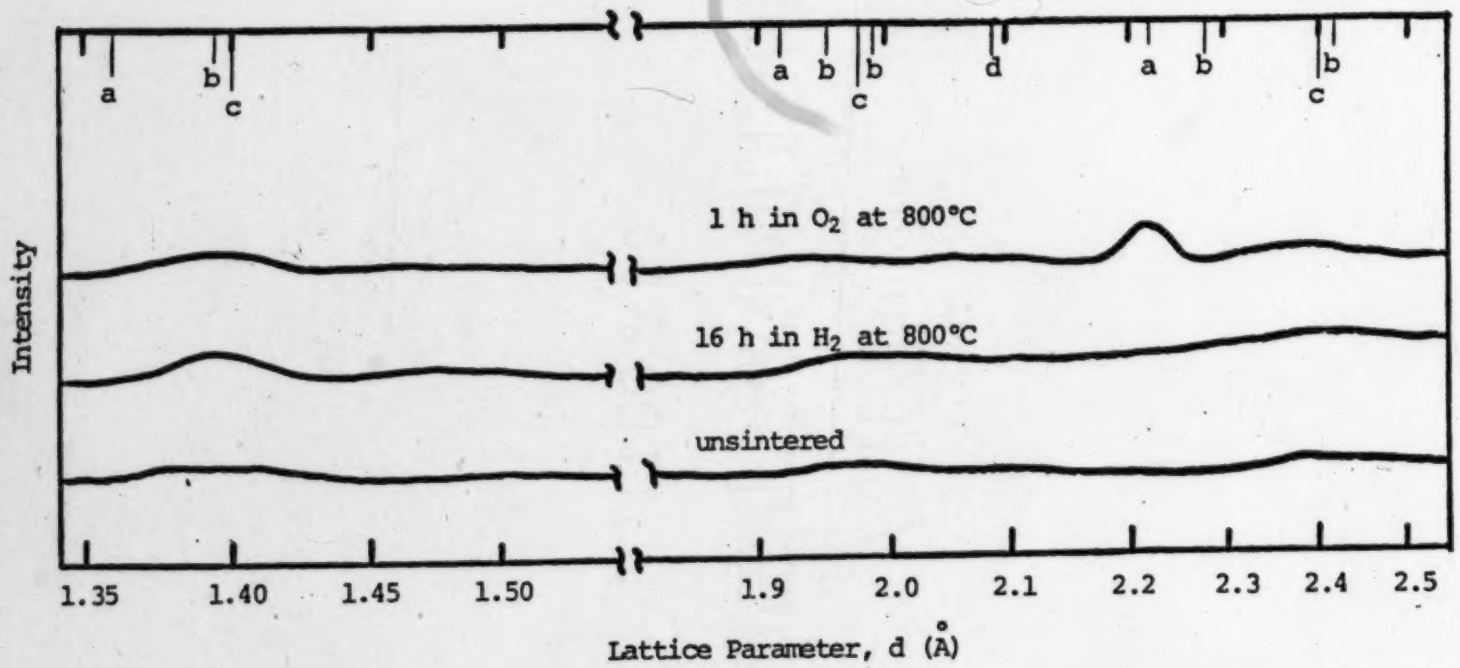

Figure 4.7: X-ray diffraction patterns of 2.0% Ir/Kaiser Al_2O_3 after indicated treatments (Lines indicated correspond to: a=Ir; b=γ-Al_2O_3; c=η-Al_2O_3 and d=α-Al_2O_3.)

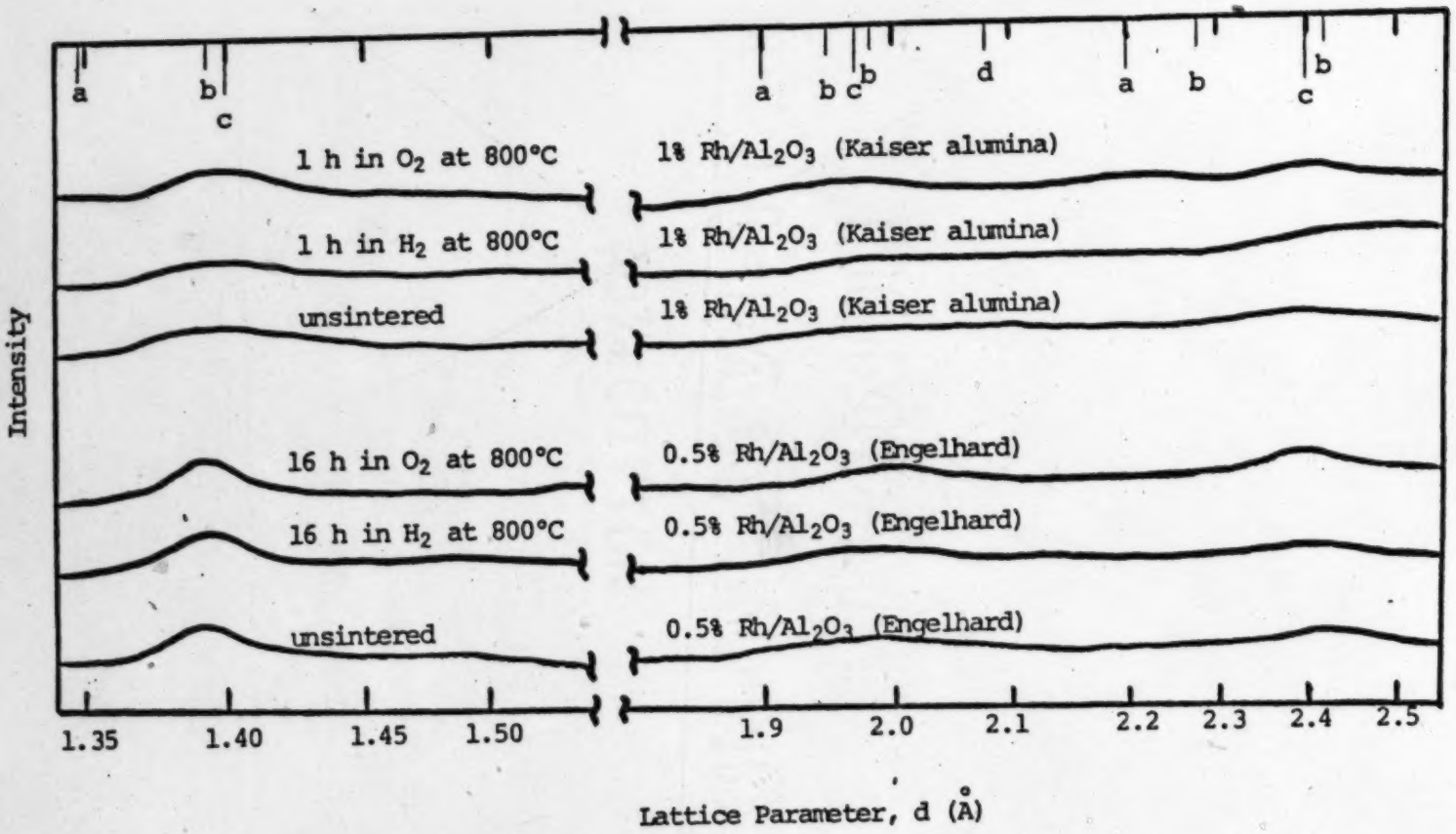

Figure 4.8: X-ray diffraction patterns of Rh/Al_2O_3 catalysts after indicated treatments. (Lines indicated correspond to: a=Rh; b=γ-Al_2O_3; c=η-Al_2O_3 and d=α-Al_2O_3.)

treatments. All the Al_2O_3 supports (unsintered and sintered) display diffuse peaks corresponding to γ-Al_2O_3 (or possibly η-Al_2O_3). For some of the heavily sintered samples, diffraction lines corresponding to the metals were observed. These lines were absent from all the unsintered samples.

The thermal treatments did result in changes in support surface area as determined by the BET method. The changes in surface area did not depend on the sintering atmosphere and the supported metal but only on the temperature and time of treatment. The results are summarized in Table 4.3. Where more than one determination on the same support material but different sintering atmosphere was carried out, the standard deviation is given in Table 4.3. These results show that for the catalysts supported on Kaiser alumina, no appreciable changes in support surface area occur during treatment for $\leq$ 16 hours at temperatures $\leq$ 600°C. For the Englehard catalysts the support surface area is approximately constant for treatment at temperatures $\leq$ 700°C. The high thermal stability of this support is probably due to calcination of these catalysts at an elevated temperature by the manufacturer. Corrections to the measured dispersions due to decrease in support area are discussed in a later section.

4.2.3 Platinum on Various Supports

4.2.3(a) Pt Supported on Gamma Alumina

Laboratory prepared 1% Pt/γ-alumina catalyst was used in this study. The catalyst had an average initial dispersion of 0.27. The normalized Pt dispersion versus temperature for different times in oxygen and hydrogen atmospheres are plotted in Figure 4.9. The treatment in oxygen at temperatures $\leq$ 600°C results in appreciable increases in

TABLE 4.3

Support Surface Areas as a Function of Thermal Treatment

Catalysts	Treatment Temp (°C)	Treatment Time (h)	Number of Determinations	Average Specific Surface Area (m^2/g)
Kaiser KA 201 alumina supported catalysts (Cat. 2, 3, and 5)	unsintered*		4	213 (±19)
	600	16	3	211 (±21)
	700	16	2	180 (± 3)
	800	1	4	157 (± 3)
	800	16	2	135 (± 1)
Engelhard Catalysts (Cat. 1, and 4)	unsintered*		4	103 (± 9)
	700	16	2	104 (±10)
	800	1	1	92
	800	4	1	84
	800	16	2	84 (± 7)

* unsintered catalysts had undergone standard pretreatment and hydrogen adsorption measurements.

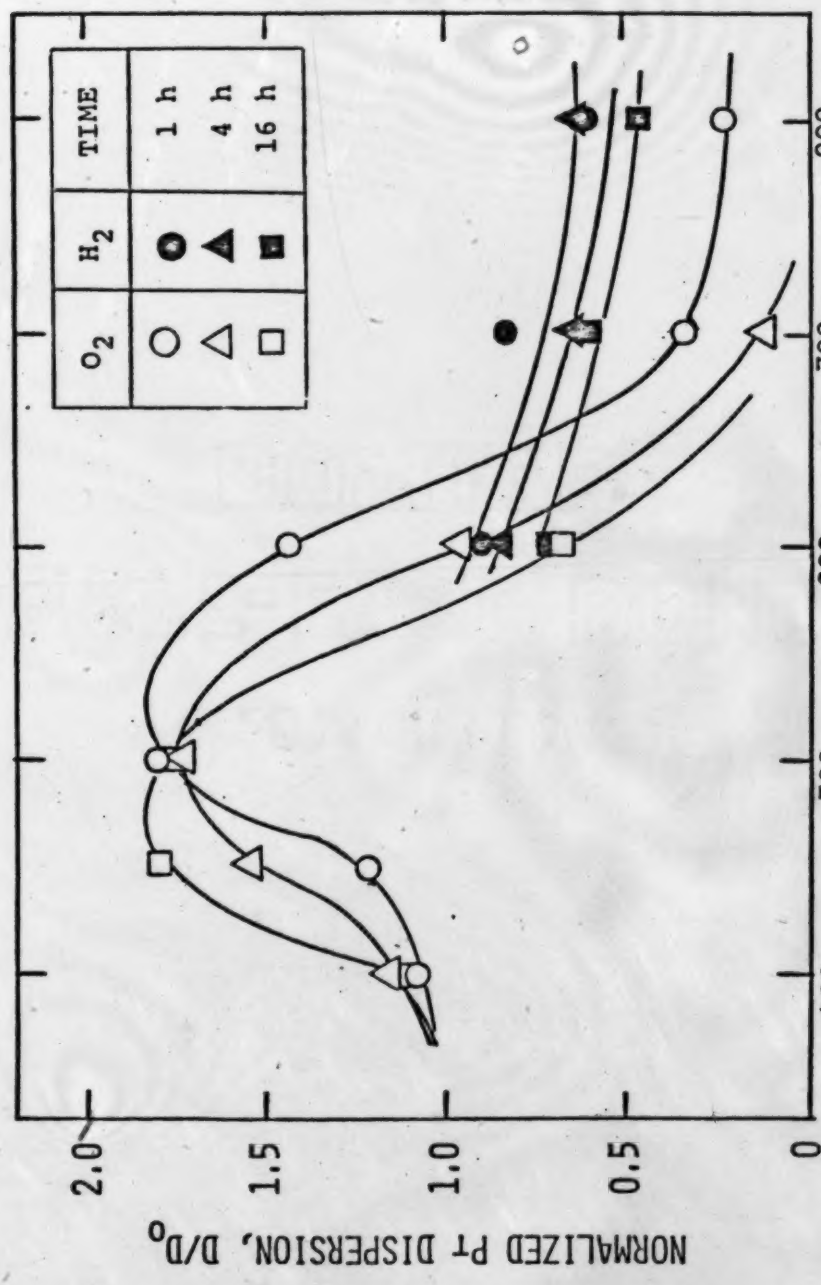

Figure 4.9: Effect of treatment in oxygen and hydrogen on the normalized dispersion for 1.0% Pt/γ-alumina.

dispersion. The maximum dispersion, which is about 1.8 times the initial dispersion, is observed at 500°C. At this temperature the increase in dispersion is approximately independent of the treatment time. Treatment at 600°C in oxygen for 1 hour resulted in a 50% increase in dispersion, but increasing the sintering time at 600°C to 16 hours resulted in ~30% decrease in dispersion. Treatment at 700°C for 4 hours resulted in more than 80% decrease in dispersion.

The treatments in hydrogen always resulted in decrease in dispersion. The treatment at 800°C for 16 hours resulted in ~ 55% decrease in dispersion. The sintering behavior of support Pt on γ-alumina is very similar to that of supported Pt on Kaiser alumina and commercial Pt/Al_2O_3 catalyst (see Figure 4.1 and 4.2). The Pt/γ-alumina catalyst seems to be a less stable catalyst in oxygen compared to the other two Pt/Al_2O_3 catalysts but in hydrogen, all three catalysts show some degree of stability. Results of the $Pt/\gamma\text{-}Al_2O_3$ catalyst are used as reference for comparison with other supports.

4.2.3(b) Pt Supported on Silica-Alumina

Figure 4.10 shows the sintering behavior of 1% Pt on silica-alumina in hydrogen and oxygen atmospheres. The composition of the support as supplied by the manufacturer was 45% alumina and 53% silica. The average initial dispersion of platinum was 0.170. Treatment in oxygen at 400°C does not lead to much change in dispersion of the catalyst. Treatment time at this temperature is unimportant because even after 16 hours of treatment the dispersion is close to initial value. The normalized dispersion, D/D_o, was just slightly more than 1 after treatment at 400°C, but it decreased rapidly as the temperature of treatment was increased. At higher temperatures, the longer time

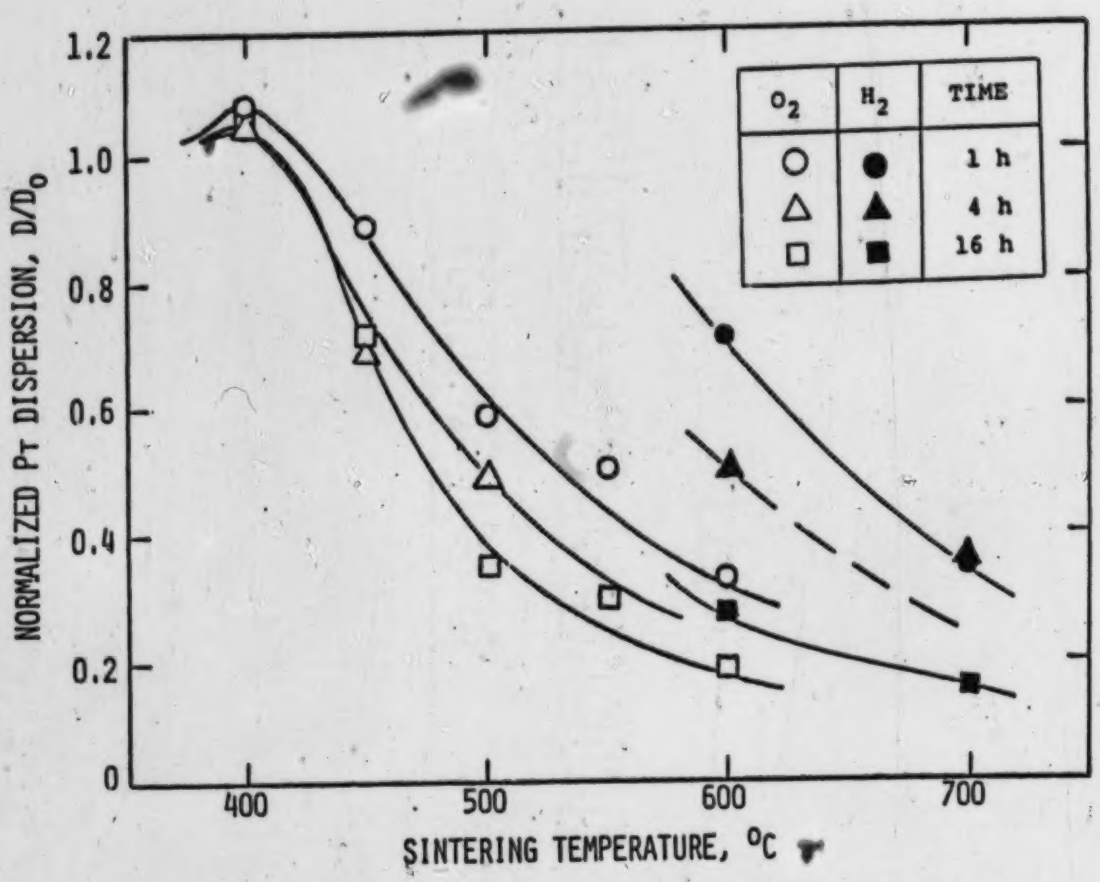

Figure 4.10: Effect of treatment in oxygen and hydrogen on the normalized dispersion for 1.0% Pt/Silica-alumina.

of treatment leads to larger decreases in dispersion. At 500°C, treatments for 1 and 16 hours resulted in decreases in dispersion of ~ 40 and 65%, respectively. The treatment time of 16 hours at 600°C resulted in more than 80% decrease in metal surface area.

Treatment in hydrogen also results in steady decreases with increase in temperature and length of exposure. Treatment times of 1, 4 and 16 hours at 600°C lead to approximately 28, 53 and 75% losses in metal dispersion. This difference becomes significantly less as the temperature of treatment increases from 600 to 700°C,

4.2.3(c) Pt. Support on Granular Silica Gel

The 1% Pt/silica gel catalyst used in this study was prepared in the laboratory by impregnation resulting in an average initial Pt dispersion of 0.130. The normalized dispersion as a function of temperature, time and type of atmosphere is plotted in Figure 4.11.

Treatment in oxygen at 400°C for 1 hour results in 17% increase in dispersion, but as the time of treatment is increased to 4 and 16 hours, the dispersion decreases and after 16 hours treatment its value is about 95% of the initial value. A similar kind of behavior is observed on treatment of the catalyst at 500°C in oxygen. Treatment at this temperature for 1 hour does not change the metal dispersion by any significant amount (an increase of ~ 5%) but as the time of exposure increases to 4 and 16 hours, the dispersion decreases by 10 and 50%. At higher temperatures (~ 550°C), the dispersion decreases very rapidly even for short treatment times.

The catalyst is slightly more stable in hydrogen than in oxygen, but treatment in hydrogen always resulted in continuous decreases in dispersion. The sintering behavior of Pt/silica gel is similar to that

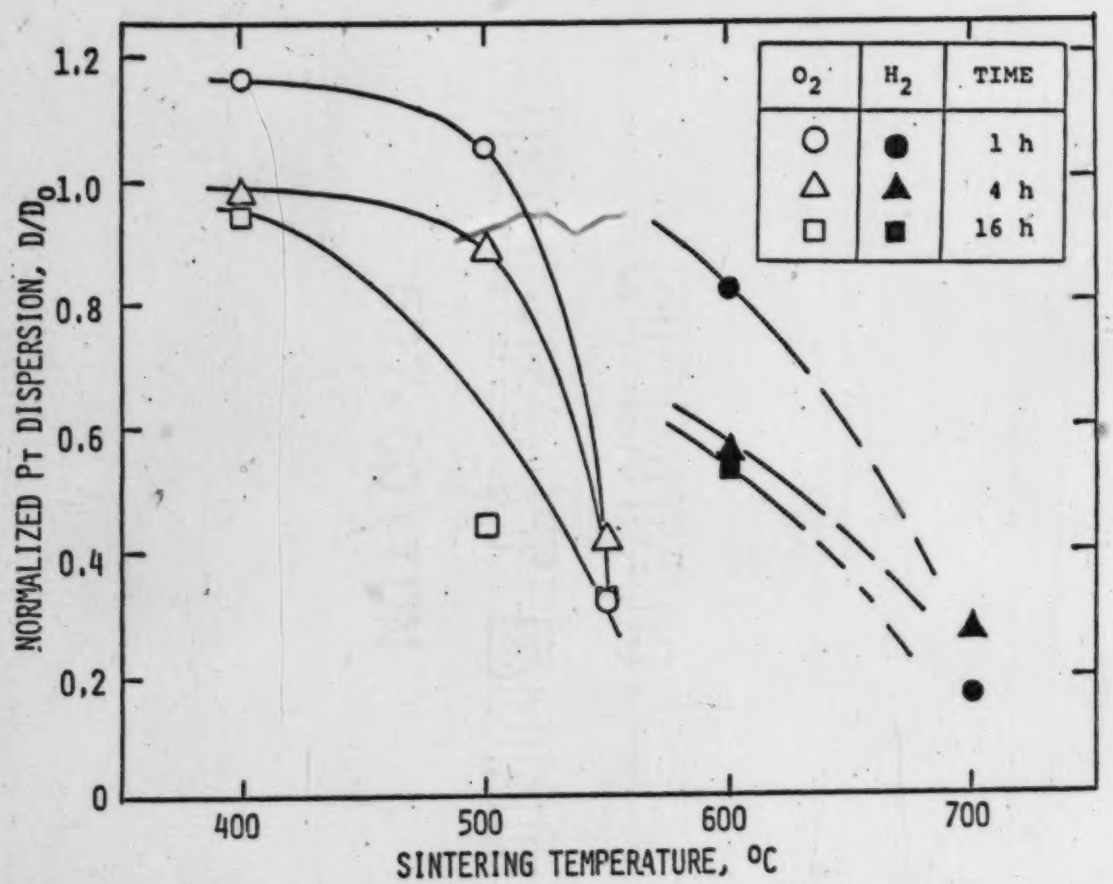

Figure 4.11: Effect of treatment in oxygen and hydrogen on the normalized dispersion for 1.0% Pt/Silica gel.

of Pt/silica-alumina in hydrogen atmosphere. One hour of treatment in hydrogen at 600°C results in a catalyst with about 80% of the initial dispersion. But increasing the time to 4 hours and 16 hours reduces the metal surface area by ~ 50% for both cases. At higher temperatures the difference in dispersion values for different times of treatment at the same temperature becomes small. An exception to the monotonic decreases in dispersion on increasing the length of time of exposure in hydrogen at the same temperature occured at 700°C for both Pt/silica gel and Pt/silica-alumina catalysts. When the time of treatment at 700°C was increased from 1 to 4 hours, the dispersion for both catalysts increased slightly. This was probably due to traces of oxygen diffusing into the sample tube during the time between experiments.

4.2.3(d) Effect of Thermal Treatment on Support Properties

The X-ray diffraction studies on unsintered and sintered samples showed (Figure 4.12) that no detectable changes occurred in the support crystalline structure. Diffused and small peaks of Pt appeared on the diffraction patterns of heavily sintered samples. The silica-alumina and silica-gel did not show the presence of any kind of crystalline structure in both unsintered and sintered samples. These supports are assumed to have an amorphous structure.

Table 4.4 lists the support surface areas for all three catalysts before and after sintering as obtained by the BET method. There was no appreciable change (< 5%) in the surface area of γ-alumina for the catalyst sintered both in oxygen and hydrogen. For silica-alumina, the catalyst sintered at 700°C for 4 hours had almost the same surface area (100 m^2g) as that of unsintered sample. An unexpected increase in area was observed for silica gel with increase in treatment

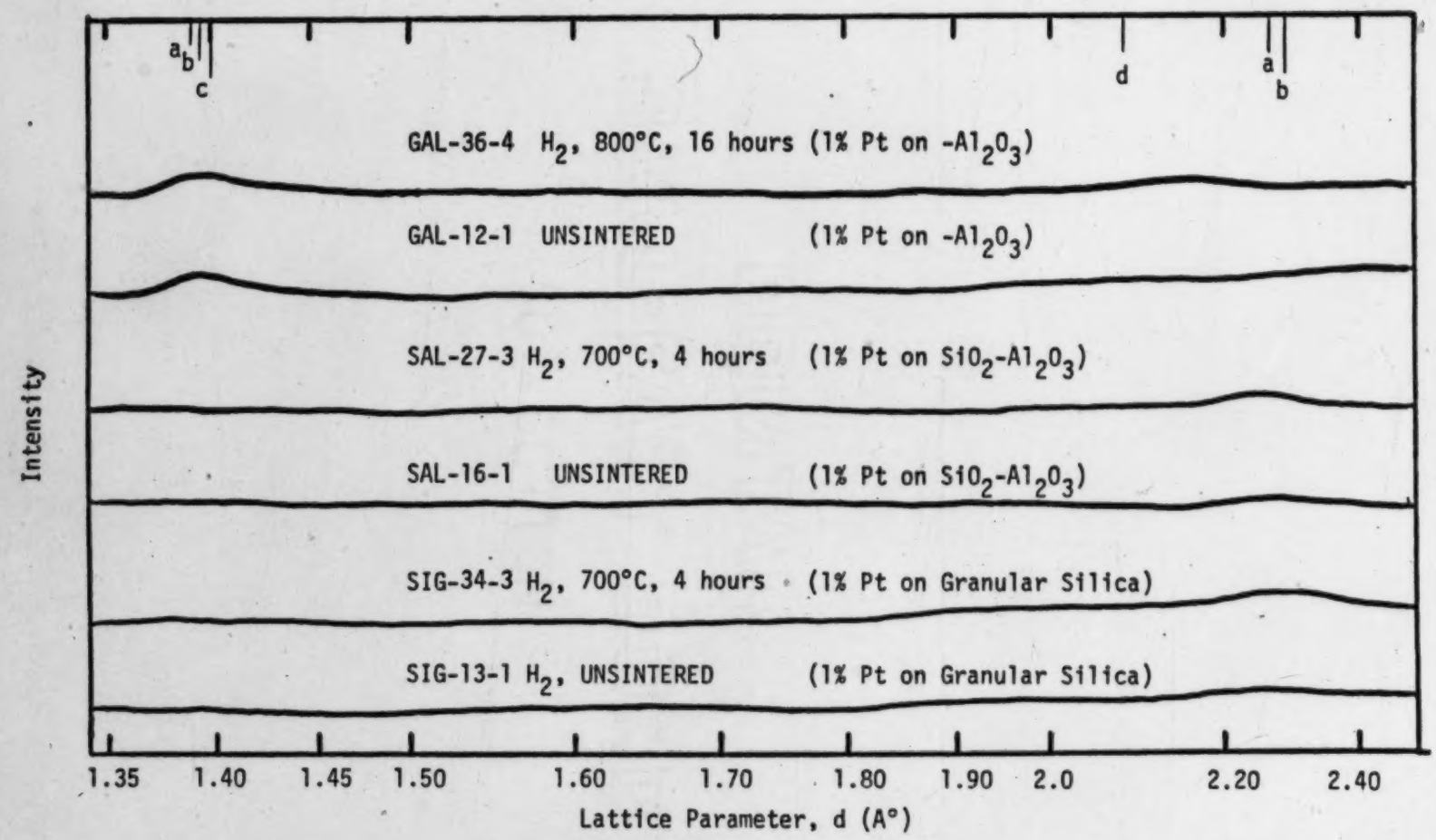

Figure 4.12: X-ray diffraction patterns of 1% Pt on Gamma Alumina, Silica-Alumina and Silica Gel (granular). (Lines indicated correspond to: a=Pt; b=γ-Al_2O_3; c=η-Al_2O_3; and d=α-Al_2O_3).

TABLE 4.4

Support Surface Areas

Sample Identification	Catalyst	Treatment	Surface Area (m^2/g)
SIG-17-1	1% Pt on silica gel	unsintered	220
SIG-20-4	1% Pt on silica gel	O_2, 550°C, 9 hours	246
SIG-34-3	1% Pt on silica gel	H_2, 700°C, 4 hours	275
SAL-18-1	1% Pt on silica-alumina	unsintered	100
SAL-27-3	1% Pt on silica-alumina	H_2, 700°C, 4 hours	100
GAL-12-1	1% Pt on γ-alumina	unsintered	73
GAL-24-4	1% Pt on γ-alumina	O_2, 600°C, 16 hours	73
GAL-36-4	1% Pt on γ-alumina	H_2, 800°C, 16 hours	70

temperature. The unsintered sample had a support surface area of 220 m^2g in comparison with 240 m^2g of a sample sintered at 550°C for 9 hours in oxygen and 275 m^2g of another sample treated at 700°C for 4 hours in hydrogen. This unexpected increase in surface area of silica gel is probably due to availability of more pores for nitrogen adsorption caused by the dehydration of silica gel on exposure to high temperatures. The atmosphere of sintering does not seem to influence the support surface area for any of the three supports studied.

4.3 Discussion

4.3.1 Interpretation of Results

Although the reproducibility of hydrogen adsorption measurements was good (See Section 4.2.1), the results for several runs listed in Table B-2 were not included in the previously presented Figures. The results for runs SIG 27 1, 2, 3 and 4 were omitted because they did not agree with any of the observed trends for supported Pt, *i.e.* sintering at 460°C in oxygen for these runs resulted in normalized dispersions that were lower than the normalized dispersions for sintering at 400 and 500°C. Runs GAL 32 3 and 4 were not used because the Pt dispersions increased significantly when treatment time in H_2 at 600°C was increased from 1 to 4 and 16 hours. The cause of this unusual behavior may have been due to accidental exposure of the sample to air between treatments. Most of the dispersions obtained for several repeated sintering experiments carried out after the treated catalysts had been exposed to air, were not used in the normalized dispersions previously presented. The runs not included

for this reason were Pt 19 1, 3R, 3R/2, PT 20 1, 7R, PT C 1, D, PT D 1, PT D 2, PT D 3, 18H, PT 18H 1, PT 18H 2, B, PT AB 1, PT AB 2, PT AB 3, IR 86 1, IR 98 1, IR 107 1 and IR 87 1.

The results for runs SAL 4 1 and 2 were not used because the initial dispersion was not measured. The large variations in initial dispersions for the same catalyst (See Table 4.1 and Section 4.2.1) is one of the limiting factors in the present work. It is largely due to this limitation that the following discussion of the results is qualitative in nature and the fitting of the data by rate functions was not attempted.

4.3.2 Sintering Behavior of Different Metals

4.3.2(a) Supported Platinum

The experimental results on sintering of supported platinum in oxygen can be summarized as follows: (1) the dispersion increased at low treatment temperature ($\leq$ 600°C); (2) at low temperatures ($\simeq$ 500 - 550°C), the dispersions were relatively independent of time; and (3) the dispersion decreased at higher temperatures ($\geq$ 650°C). These changes in dispersion resulting from treatment in oxygen have been discussed previously by Fiedorow and Wanke (14). According to their interpretation the transport of metal at sintering temperatures occurs mainly by the movement of PtO_2 species on the support surface. Their explanation of the sintering behavior of supported platinum in oxygen is consistent with the predictions of atomic migration model. The various processes by which transport of Pt can occur are discussed in detail in reference (14).

Treatment in hydrogen resulted in monotonic decreases in metal surface area with increasing sintering temperatures. This is contrary to recent results reported by Hassan *et al.*(38). These investigators report a decrease in Pt surface area due to treatment in hydrogen at temperatures below 400°C and an increase at temperatures above 400°C. They also report a steady decrease in metal surface area with increasing treatment temperature in oxygen atmospheres. These types of behavior were never observed in this study nor in the several hundred sintering experiments carried out in this laboratory using alumina supported Pt.

4.3.2(b) Supported Iridium

The results presented in Figure 4.3 show that supported Ir is considerably more stable in hydrogen than in oxygen atmospheres. Treatment in hydrogen for 16 hours at 800°C resulted in a 20% decrease in dispersion. This is less than the decrease in support surface area (34%) for these treatment conditions. Hence it can be concluded that the loss in Ir dispersion for treatment in hydrogen at temperatures up to 800°C and 16 hour periods is mainly due to collapse of the support pore structure.

The higher volatility of Ir oxides compared to Pt oxides (37, 38) is probably the cause of the low stability of supported Ir in oxygen. The higher volatility of Ir oxides causes redispersion at lower temperature range for Ir (300 to 400°C) compared to that for

Pt (300 to 600°C). This is also the reason for the rapid decreases in dispersion at temperatures >400°C. Due to the relatively high vapor pressure of IrO_3 (37), it is possible that vapor phase transport contributed significantly to the decreases in measured dispersions after oxygen treatments at 700°C and 800°C. Vapor transport can decrease the measured dispersion by causing crystallite growth as well as by decreasing the Ir content of the catalysts.

4.3.2(c) Supported Rhodium

The supported rhodium did not show any appreciable increase in dispersion due to treatment in oxygen. The attempts to redisperse sintered samples by treating them in oxygen at 500°C did not result in significant changes in dispersion. Comparison of Figures 4.4 and 4.5 for 1 hour sintering leads to the conclusion that 1% Rh is less stable than 0.5% Rh in oxygen even after the larger loss of support surface area for the 1% Rh catalyst is taken into account. But the situation is reversed for treatment in hydrogen, *i.e.*, the 1% Rh catalyst appears to have a greater thermal stability than the 0.5% Rh catalyst.

Examining the changes in support surface area due to thermal treatment (Table 4.3) leads to the conclusion that the loss in Rh dispersion for 1% Rh catalyst is mainly due to loss in support area which would make some of the Rh inaccessible to hydrogen during adsorption. For 0.5% Rh, the loss in support surface area is insufficient to account for the total loss in dispersion (*e.g.* sintering at 800°C for 16 hours resulted in a 41% decrease in dispersion while the support surface area decreased only 18%).

Differences in the initial crystallite size distributions, support metal interactions and metal loading could all be responsible for the different behavior of the two Rh catalysts. It is impossible on the basis of the data obtained in this work to determine which, if any, of these factors are the cause of the observed behavior.

4.3.3 Comparison of Stability of Supported Metals

It is difficult to compare the stability of different catalysts since various factors can influence the stability. These factors include the initial dispersion, the crystallite size distribution, the metal loading and the nature of support. In order to compare the stability of catalysts in oxygen and hydrogen as a function of temperature all these factors should be kept constant. Unfortunately, it is in general, not possible to obtain constant initial conditions for the catalysts.

An approximate method for obtaining the relative stabilities of various catalysts is to compare relative change in dispersion, *i.e.* compare normalized dispersions. Correction for the change in support surface area should also be made. The result of these corrections are shown in Table 4.5. In making these corrections it was assumed that the loss in support surface area is proportional to the loss in accessible metal. This procedure probably overestimates the fraction of metal which becomes inaccessible to hydrogen because nitrogen was used in the BET surface area measurements and some of the internal pore structure after sintering may be accessible to hydrogen but not

TABLE 4.5

Effect of Changes in Support Surface Area on Dispersion

Catalyst	Treatment Conditions: 700°C and 16 h $(\frac{D}{D_o})$	700°C and 16 h $(\frac{D}{D_o})(\frac{S_o}{S})$*	800°C and 1 h $(\frac{D}{D_o})$	800°C and 1 h $(\frac{D}{D_o})(\frac{S_o}{S})$	800°C and 16 h $(\frac{D}{D_o})$	800°C and 16 h $(\frac{D}{D_o})(\frac{S_o}{S})$
Treatment in Hydrogen						
4	-	-	0.54	0.60	-	-
3A	0.47	0.56	0.53	0.72	0.37	0.58
5	0.82	0.97	0.82	1.11	0.80	1.26
1	0.78	0.78	0.74	0.83	0.59	0.72
2	-	-	0.73	0.99	-	-
Treatment in Oxygen						
4	-	-	0.16	0.18	-	-
3	0.40	0.47	0.14	0.19	-	-
5	(<0.02)	(<0.02)	0.046	0.06	(~0.00)	(~0.00)
1	0.63	0.63	0.49	0.55	0.21	0.26
2	-	-	0.24	0.33	-	-

* S_o and S are the specific surface areas of the support for unsintered and sintered samples listed in Table 4.3.

to nitrogen. It is believed that this is the reason that some of the normalized dispersions corrected for loss in surface area exceed unity for the Ir catalyst.

Based on the results presented in Figures 4.1 to 4.5 and Table 4.5, the order of decreasing stability is

$$Rh > Pt > Ir \qquad (4.1)$$

in oxygen and

$$Ir > Rh > Pt \qquad (4.2)$$

in hydrogen.

The sequence of stability in oxygen given by Equation 4.1 is in agreement with the predictions of Wynblatt and coworkers (34, 39). The predictions of relative stability of metals in oxygen were based on the heats of formation of metal oxides; increases in the exothermicity of the metal oxide formation is postulated to cause decreases in the stability. Hence, it can be concluded that the sintering for all these supported metals occurs by the transport of metal oxide species. The possible steps involved in the transport of metal oxides has been discussed previously by Fiedorow and Wanke (14). The prediction of Wynblatt and coworkers (34, 39) for the relative stability in hydrogen atmospheres is not in complete agreement with the sequence given in Equation 4.2. It was found that the supported Rh catalysts were considerably more stable than the supported Pt catalysts. According to predictions, which are based on the premise that in hydrogen stability increases with increasing heat of sublimation of the metal, the stabilities of Rh and Pt should be approximately equal.

It may be argued that the stability sequence based on relative changes in dispersion yields wrong results due to different initial conditions (such as initial disperion and crystallite size distribution) for the Pt and Rh catalysts. This is not the case since catalysts with high initial dispersions generally have larger decreases in relative dispersions than similar catalysts (same support and metal loading) with lower initial dispersions. The initial dispersions of both Rh catalysts were in general higher than those of Pt catalysts. The deviations from the predictions are believed to be caused by metal-support and/or metal-hydrogen interactions. The predictions do not include these interactions which, in the opinion of the author, play an important role in the sintering of supported metal catalysts.

4.3.4 Effect of Supports on Sintering Behavior of Pt

The sintering behavior of platinum supported on γ-alumina was found to be very similar to that of platinum supported on Kaiser alumina. Treatment in oxygen at $\leq$ 600°C resulted in increases in dispersion. At 500°C the time of sintering in oxygen had only a minor effect on the resulting dispersion, but at 450°C, the 4 and 16 hour treatments resulted in a continuous increase in dispersion. The maximum increase in case of γ-alumina ($\sim$ 80%) was less than that for Kaiser alumina ($\sim$ 150%). The Pt supported on the γ-alumina appears to be less stable than the Pt supported on the Kaiser alumina during treatment in oxygen (cf. Figures 4.1 and 4.9). Comparing the changes in normalized dispersion for these two catalysts due to treatment in hydrogen in Figures 4.1 and 4.9 indicates that the 1% Pt/γ-alumina catalyst is the more stable catalyst, *e.g.* treatment in hydrogen for 16 hours at 800°C decreased the normalized dispersion for the Kaiser alumina supported

catalyst by 64% while for the γ-alumina supported catalyst the decrease is only 53%. But when decreases in support surface area due to 16 hour of treatment at 800°C are taken into account (37 and 5% for Kaiser alumina and γ-alumina, respectively), the decreases in accessible Pt surface areas are approximately the same for the two catalysts.

The X-ray diffraction patterns of Kaiser alumina showed slightly more changes in its crystallinity than the γ-alumina (*cf.* Figures 4.6 and 4.12). The differences in the behavior of these two supports may be due to factors other than differences in support crystalline structure. These factors could include metal loading, initial PSD and dispersion, initial support surface area etc. It is difficult to say which one of these is more important than others. However, despite all these factors the behavior of Pt supported on γ-alumina and Kaiser alumina was very similar and it is safe to assume that sintering of Pt on both these supports occurs by the same mechanism. Since the metal loading of Pt on γ-alumina, silica-alumina and silica gel was the same, the results of sintering of Pt on γ-alumina will be compared with the sintering results of Pt on silica-alumina and silica gel.

Treatment in oxygen of Pt on silica-alumina and silica gel did not result in significant increases in dispersion for temperatures $\leq$ 500°C. The maximum increase observed was $\sim$17% for silica gel on treatment at 400°C for 1 hour. There was virtually no increase in metal dispersion observed for Pt on silica-alumina at any temperature. At lower temperatures the metal dispersion was less dependent on treatment time for silica-alumina compared to silica gel, but at higher temperatures the longer treatment times generally resulted in

lower dispersion for the silica-alumina supported catalyst. Both supports exhibited similar behavior on treatment in hydrogen. There was a steady decrease in metal dispersion observed with increasing treatment times and temperatures for both supports. Both silica gel and silica-alumina were a more stable support in hydrogen than in oxygen. From the results of this study, it is very difficult to say which one of these two is a better support. Losses in relative metal dispersion were of the same order for both supports in both types of atmospheres. The average initial dispersions of the silica gel and silica-alumina catalysts were considerably lower than the initial dispersion of the γ-alumina catalyst, (0.13 and 0.17 compared to 0.27).

The role of the support surface area and the initial Pt dispersion should be considered when comparing the results for the three different supports used in this work. Assuming all other factors being equal, then high surface area support should result in catalyst with higher thermal stability. This behavior is predicted by both crystallite and atomic migration mechanisms. Catalysts with high metal dispersions should be less stable, using normalized dispersion as the criterion for stability, than catalysts with lower initial dispersion.

In light of these general predictions and the results presented, it is concluded that silica gel (highest support area and lowest initial dispersion) is the worst of the three supports studied. Gamma-alumina (lowest support area and highest initial dispersion) is the best of the three supports, *i.e.* thermal treatment in both oxygen and hydrogen for γ-alumina supported Pt resulted in smaller decreases or larger increases in dispersions than similar treatments for Pt.

supported on silica-alumina or silica gel.

4.3.5 Comparison of Experimental Results with Theoretical Predictions.

One of the major reasons for undertaking this study was to obtain data on the basis of which it would be possible to discriminate between the two sintering mechanisms. Therefore an attempt will be made to explain the observations in terms of mechanistic models. Two mechanistic models which have been proposed for the sintering processes were described in Chapter 2. The results will be discussed in terms of each model separately.

4.3.5(a) Crystallite Migration Model

The crystallite migration model always predicts increases in average crystallite sizes, *i.e.* decreases in dispersion, as sintering proceeds. To account for increases in dispersion, an additional process of splitting of metal crystallites was postulated by Ruckenstein and Pulvermacher (30). The break-up of Pt films on α-alumina substrates into Pt crystallites during treatment in air at 500° to 1000°C has been observed (12, 33), but substrates completely covered by a metal film of 5 to 20 mm thickness is a considerably different situation than one encounters in supported metal catalysts. In supported metal catalysts the fraction of the support surface covered by metal is usually <1%, *e.g.* 0.7% of the support area is covered by Pt in a 2% Pt/Al_2O_3 catalyst with a support surface area of 200 m^2/g and an average crystallite size of 2 nm. The splitting of Pt films has been observed only above 500°C, while in the present study, the increases in dispersion were observed at temperatures as low as 300°C

(Figure 4.3). Also the break-up of crystallites in these studies yielded particles with diameters generally above 7 nm, while for a Pt catalyst with a dispersion of 0.5, the average crystallite size is approximately 2 nm. Whether the break-up of the films was dependent on time is not reported in these studies. According to the splitting theory, the increases in dispersion should be independent of the surface area of the support, the metal loading and the initial metal crystallite size. The dependency of increases in dispersion on metal loading was studied by Fiedorow and Wanke (14). They found that the higher the metal loading, the smaller the increases in dispersion, which is contrary to the predictions of the crystallite migration - crystallite splitting model. Assuming that the difference between three alumina supports used in this study is not very significant, the dispersions for all three catalysts according to the splitting theory, should be approximately equal after a specific oxygen treatment. The maximum dispersions obtained after redispersion varied more than a factor of two. This is again contrary to predictions of crystallite migration-crystallite splitting model.

The sintering results obtained for treatment in hydrogen can possibly be explained by the crystallite migration model since continuous decreases in dispersion were observed. Nevertheless, it is difficult to rationalize the high thermal stability of the Rh and Ir catalysts in hydrogen on the basis of the crystallite migration model. The motion of crystallites in this model is postulated to be caused by surface diffusion of metal atoms on the surface of the metal crystallites (34) and this would indicate that the mobility of Rh crystallites would be approximately equal to that of Pt crystallites

resulting in a similar stability for Pt and Rh. This was not observed. The exceptionally high thermal stability of the Ir catalyst is also difficult to explain since the surface diffusivity of Ir at 800°C is expected to be of the same order of magnitude as the surface diffusivity of Pt at 600°C based on the argument that surface diffusivity is proportional to $e^{-T_m/T}$ where T_m is the melting temperature (34). The loss of dispersion of Pt at 600°C was greater than that of Ir at 800°C if losses in support area are taken into account. All observations of this study lead to the conclusion that crystallite migration is not the major mechanism for sintering of supported metal catalysts.

4.3.5(b) Atomic Migration Model

The atomic migration model predicts decreases as well as increases in dispersion depending on the treatment conditions. Increases in dispersion result if the migrating species are trapped at sites on the support that have large metal-support interactions or if colliding molecular species result in the nucleation of new crystallites.

For platinum-oxygen-support system, the transport of Pt occurs mainly by PtO_2 species. The various possible routes which result in increases in dispersion are described in detail by Fiedorow and Wanke (14). This mechanism is able to explain the behavior of supported platinum in oxygen. The only drawback with the mechanism is that some of the possible routes used in this sintering mechanism are not well understood energetically and work should be done to define these routes and their energetics. The Ir catalysts also possibly sinter with the same mechanism in the presence of oxygen, but

because the volatility of iridium oxides is considerably higher than that of PtO_2, the vapor phase transport could be more important. This is probably the reason for the low stability of Ir catalysts in oxygen. In the case of Rh catalysts, the results can be explained on the basis of assumption that the rhodium-oxygen interactions are not very large and therefore the main transport of rhodium probably occurs by rhodium atomic species. The heat of formation of rhodium oxide is known to be higher than Pt and Ir. Therefore, the prediction of Wynblatt and coworkers (34, 39), about relative stabilities in oxygen, based on these heats of formation of oxides, is in agreement with the results obtained in this study.

The atomic migration model predicts a continuous decrease in dispersion if the support-migrating species interactions are small. The migrating species during treatment in hydrogen are the metal atoms. The activation energy required for the movement of atoms away from crystallites would be higher in case of treatment in hydrogen because of the absence of oxide forming step (28). For this reason the catalysts were generally more stable in hydrogen than in oxygen. The rhodium catalysts were the only exception to this observation. But this can be explained by the following argument. The absence of large interactions between migrating species and support caused the catalyst to be fairly stable in both the atmospheres. The transport occured mainly by atomic rhodium in both oxygen and hydrogen. The exceptional stability of Ir catalysts in hydrogen can be argued to be the result of the high activation energy required to move iridium atoms from metal crystallites which is supported by the fact that Ir has a high sublimation energy.

The absence of significant redispersion for the Pt/silica gel and Pt/silica-alumina catalysts could be due to the low initial dispersions of these catalyst or due to support-Pt oxide interactions which are less than the alumina-Pt oxide interactions. At present the author favours the second explanation, but further experiments are necessary to substantiante this belief.

On the basis of the above mentioned observations, it can be said that for sintering in oxygen, predictions of atomic migration model are in agreement with observed results. The crystallite migration model fails to explain many observed phenomenon. The sintering in hydrogen could take place by either mechanism, but the experiments of Baker *et al.*(35) have shown that the sintering of alumina supported Pt in hydrogen occurs by particles smaller than 2.5 nm. This again supports the atomic migration model since for dispersions < 0.4 the average crystallite size is > 2.5 nm. For most of the sintering in hydrogen in the present work, D was < 0.4.

Experiments to determine the effect of initial dispersion on the increase in dispersion during oxygen treatment and the effect of support surface area on sintering behavior should be conducted. Also, experiments on thermal stability of supported alloy catalysts would further the understanding of the sintering mechanism.

CHAPTER 5

CONCLUSIONS

Based on the data obtained in this study, the following conclusions were made:

1. The stability sequence of alumina supported metal catalysts for sintering in oxygen is Rh > Pt > Ir.
2. The stability sequence of alumina supported metal catalysts for sintering in hydrogen is Ir > Rh > Pt.
3. Gamma alumina is a better support for Pt than silica-alumina and silica gel.
4. Treatment in oxygen of Pt/Al_2O_3 catalysts at temperatures <600°C results in increases in Pt dispersion.
5. Treatment in oxygen of Ir/Al_2O_3 at $T \leq 400°C$ and periods of ≤ 1 hour results in increases in Ir dispersion.
6. Treatment of Rh/Al_2O_3 catalysts in oxygen does not result in increases in dispersion.
7. Treatment of Pt on silica-alumina and silica gel in oxygen does not result in significant increases in dispersion.
8. Treatment in hydrogen of supported Pt, Ir and Rh does not result in increases in metal dispersion.
9. The sintering mechanism for support Pt, Ir and Rh in oxygen atmospheres is the migration of molecular and/or atomic species and not the migration of metal crystallites.

10. The sintering mechanism for supported Pt, Ir and Rh in hydrogen atmospheres is probably the migration of metal atoms, but the migration of metal crystallies cannot be ruled out as a contributing factor.

CHAPTER 6

RECOMMENDATIONS

The variation in initial dispersion among samples taken from the same batch of catalyst was the limiting factor in the reliability of the data obtained in the present study. It is recommended that different impregnation or ion exchange techniques be investigated with the aim of finding catalyst preparation techniques which result in improved catalyst homogeneity.

Another factor which affected the reliability of the reported normalized dispersions was the loss of support surface area due to thermal treatment. Although qualitative corrections for this occurrence were made, the problem can be avoided if the support is calcined before impregnation at the maximum temperatures encountered during sintering. It is recommended that supports be calcined at conditions equal to or exceeding the most severe sintering conditions to be employed or that supports with stable surface areas at the sintering conditions (*e.g.* Alon) be used in future investigations.

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APPENDIX A

CALCULATION PROCEDURES

A-1 Dispersion Calculation

Hydrogen chemisorption was used to measure the dispersion. Hydrogen pulses, 18.7 μmoles per pulse, were injected into a nitrogen carrier gas stream at 3 minute intervals until two successive eluting pulses were of the same size. This indicated that no more adsorption was occuring. The areas under the peaks corresponding to the final two pulses were assumed to represent 18.7 moles of hydrogen. The fractional output of prior peaks were computed by comparing their areas with the areas of the final peaks and assuming a linear relationship between the amount of hydrogen passing through T.C. cell and the peak area. A set of sample calculations of dispersion of Pt atoms for 1% Pt on γ-alumina catalyst (for run GAL-24-2) are shown below. The sample calculations are for the first of two adsorptions carried out in this run. For most of the runs, at least two adsorption measurements were carried out and an average value of dispersion was calculated from these two measurements. In calculating the dispersion (*i.e.* the ratio of surface to total metal atoms), it was assumed that one hydrogen atom adsorbs per surface metal atom. Therefore, the dispersion is equal to the ratio of hydrogen atoms adsorbed by a sample to total metal atoms in the sample. The assumption that one hydrogen atom adsorbs per surface metal atom is questionable and for this reason the reported dispersions are normalized dispersions, D/D_o, where D_o is the dispersion of the unsintered sample. The value of D/D_o is independent of adsorption stoichiometry.

The calculations were done on Amdahl 470/VS computing system. The program used for calculations is listed in table B-3 in Appendix B.

The results obtained through this program are presented in table B-2 in Appendix B.

Sample Calculations

$$D = \text{metal dispersion} = \frac{\text{surface metal atoms}}{\text{total metal atoms}} \qquad \text{(A-1)}$$

$$\text{Total metal atoms} = \frac{(W)(X)(N_o)}{(MW)} \quad \text{[metal atoms]} \qquad \text{(A-2)}$$

$$\text{Surface metal atoms} = \text{atoms of hydrogen adsorbed} \qquad \text{(A-3)}$$

$$\text{atoms of hydrogen adsorbed} = (2)(18.7\times10^{-6})(N)(N_o)\left[\begin{matrix}\text{H atoms}\\ \text{adsorbed}\end{matrix}\right] \qquad \text{(A-4)}$$

Substituting equation A-2 and A-4 into equation A-1 yields

$$D = \frac{(37.4\times10^{-6})(N)(MW)}{(W)(X)} \qquad \text{(A-5)}$$

where

W = mass of catalyst sample [g]

X = mass fraction of metal in sample

N_o = Avogadro's number

(MW) = molecular (atomic) weight of metal [g/g mole]

N = number of hydrogen pulses adsorbed

As an illustration, the results of Run GAL-24-2 are used in the following calculations. The catalyst sample for this run was 4.745 g of 1.0% Pt/Al_2O_3 and the areas under the eluted peaks for the first adsorption are given in the table below.

TABLE A-1. Adsorption Data for Run GAL-24-2
(First Adsorption)

Pulse Number	Area under Eluted Peak	Fraction of Pulse Eluted
1	0	0.0
2	140	140/6,580 = 0.021
3	5,690	5,690/6,650 = 0.856
4	6,390	6,390/6,580 = 0.971
5	6,650	1.000
6	6,580	1.000
	Total Pulse Eluted	3.848

N = total pulse injected - total pulse eluted = 6.0 - 3.85 = 2.15
(N is always rounded off to the nearest one hundredth of a pulse).
Similar calculations for the second adsorption yields N = 2.20
Substituting the appropriate values into equation A-5 yields

$$D = \frac{(37.4\times10^{-6})(2.15)(195.1)}{(4.745)(0.010)} = 0.3306$$

for the first adsorption, and

$$D = \frac{(37.4\times10^{-6})(2.20)(195.1)}{(4.745)(0.010)} = 0.3383$$

for the second adsorption.

The average dispersion is therefore

$$D_{avg} = \frac{0.3306 + 0.3383}{2} = 0.334$$

The normalized dispersion was calculated using the above average dispersion and the dispersion for the unsintered sample (Run GAL-24-1; Table B-2). This yields

$$D/D_o = \frac{0.334}{0.232} = 1.44$$

A-2 X-Ray Diffraction Patterns

Samples for X-ray diffraction measurements were prepared by crushing the catalyst into a fine powder and sprinkling it onto a thin Vaseline coated glass slide. The range of scanning was from $\theta = 17°$ to $\theta = 35°$ at a scanning rate of 0.25° per minute using Ni filtered Cu radiation. The X-ray diffraction patterns shown in Chapter 4 were obtained by visually smoothing the recorded patterns.

A-3 Surface Area Determinations

The support surface area measurements were carried out on a constant volume BET apparatus. The dead volume determinations were done using helium. At least 4 readings of dead volume were taken for each sample and an average of all these values was used. The adsorption procedure consisted of the following steps: One, introducing adsorbate (nitrogen) to a desired pressure into the gas holder which is isolated from the evacuated catalyst holder; two, expanding the adsorbate into the catalyst holder; three, waiting for pressure to reach a steady value; four, isolating the sample holder from the gas holder; five, introducing adsorbate to a desired pressure into gas holder; and six, repeating steps two to five at least four times. The amount adsorbed at the various pressures is given by

$$V_i = \frac{1}{RT_g}\left[V_g \sum_{j=1}^{i}(P_j - P_{j-1}') - P_i'(V_g + \bar{V}_d)\right] \qquad \text{(A-6)}$$

where

V_g = volume of gas holder

$\bar{V}_d$ = average dead volume

T_g = temperature of gas holder

P_i = pressure in gas holder after i^{th} adsorbate introduction before opening valve to catalyst holder

P_i' = pressure (steady-state value) in gas holder and catalyst holder after opening valve to the catalyst for the i^{th} measurements ($P_o' = 0$)

A plot of $P_i'/[U_i(P_o-P_i')]$ vs. P_i'/P_o leads to a straight line with slope a and intercept b. P_o is saturation pressure of adsorbate (nitrogen) at the temperature of adsorption. This valve was measured with a Wallace-Tiernan pressure gauge. The slopes and intercepts were calculated by visually fitting a straight line through the data points in the range $0.05 \leq P/P_o \leq 0.35$. The monolayer coverage uptake U_m is given by

$$U_m = \frac{1}{a+b} \qquad \text{(A-7)}$$

Once U_m is known, the support surface area is calculated using the following equation:

$$A = U_m N_o A_o \qquad \text{(A-8)}$$

where A is support surface area, N_o is Avogadro's number and A_o is area covered per N_2 molecule which is taken to be equal to 15.8×10^{-20} m^2. Sample calculations are shown below:

Surface Area Sample Calculations

Experiment No.: X-2A

Sample Identification: SIG-34-3, Sintered in H_2 at 700°C for 4 hours.

Outgas Temp.: 300°C Outgas Time: 16 hours

Sample Weight:

W_1 = 5.6623 g P_o = 696 mmHg = 13.44 psia

W_2 = 4.8158 g T_o = 22°C = 295°K

W_3 = 0.8465 g

a) Dead Volume V_d Determination:

Volume of gas holder, V_g = 145.92 ml

P_1(psia)	P_2(psia)	V_d(ml) = V_g $(P_1-P_2)/P_2$
5.380	4.210	40.55
5.045	3.945	40.69
4.230	3.310	40.56
4.245	3.320	40.66

Average Vol., $\overline{V}_d$ = 40.62

b) Adsorption Data:

i	P_i(psia)	P_i'/psia	P_i'/P_o
1	2.440	0.040	0.0030
2	2.525	0.440	0.0327
3	3.580	1.685	0.1254
4	4.028	2.835	0.2109
5	5.210	4.038	0.3001
6	5.030	4.535	0.3374

c) Computation of U_m and Surface Area:

i	P_i'/P_o	$(1-P_i'/P_o)$	U_i	$P_i'/[V_i(P_o-P_i')]$
1	0.0030	0.997	9.806×10^{-4}	3.068
2	0.0327	0.9673	17.907×10^{-4}	18.878
3	0.1254	0.8746	24.263×10^{-4}	59.094
4	0.2109	0.7891	29.777×10^{-4}	89.756
5	0.3001	0.6999	33.213×10^{-4}	129.099
6	0.3374	0.6626	34.677×10^{-4}	146.843

The plot of $(P_i'/P_o0/U_i(1-P_i'/P_o)$ vs. P_i'/P_o for points i = 2 to i = 5 results in a straight line with a slope = 400.72 $moles^{-1}$ and intercept = 8.88 $(moles)^{-1}$

$$\therefore U_m = \frac{1}{400.72+8.88} \text{ moles}$$

$$= 2.44\times10^{-3}$$

$$\therefore \text{Area} = 2.44\times10^{-3}(\text{moles})\times 6.023\times10^{-23}\times158\times10^{-20}\left(\text{mole}^{m2}\right) \times \frac{1}{0.8465g} = 275\ \frac{m^2}{g}$$

APPENDIX B

EXPERIMENTAL DATA

Table B-1 describes the different catalysts used in this work, *i.e.* their composition, preparation method and identification number as used in table B-2. The experimental data, including pretreatment history, sample weight and number of pulses for each run are shown in table B-2. The runs which are identified by a '*' at the end of the run identification number were conducted by Dr. Ryszard Fiedorow. Table B-3 lists the FORTRAN program used to calculate the metal dispersions.

TABLE B-1. Identification and Description of Catalysts

Catalyst Identification No.	Catalyst Composition	Method of Preparation
1	0.5% Rh on alumina	commercial catalyst (Englehard; Lot 17-941)
2	1.0% Rh on Kaiser KA-201 alumina	impregnation with $RhCl_3$ solution
3	2.0% Pt on Kaiser KA-201 alumina	impregnation with $H_2Pt\ Cl_6$ solution
4	0.5% Pt on alumina	commercial catalyst (Englehard; Lots 18-381 and 23-288)
5	2.0% Ir on Kaiser KA-201 alumina	impregnation with $IrCl_3$ solution
6	1.0% Pt on granular silica gel[a]	impregnation with $H_2Pt\ Cl_6$ solution
7	1.0% Pt on silica alumina[b]	impregnation with $H_2Pt\ Cl_6$ solution
8	1.0% Pt on γ-alumina[c]	impregnation with $H_2Pt\ Cl_6$ solution

[a]support supplied by Alfa Products; Lot #071775

[b]support supplied by Alfa Products; Lot #081175

[c]support supplied by Alfa Products; Lot #081175

TABLE B-2

RESULTS OF SINTERING EXPERIMENTS

(pages 80 to 99)

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
ERH 44 *	1	UNSINTERED			3.0308	1.480	0.376
						1.450	0.368
					AVERAGE DISPERSION =		0.372
ERH 45 *	1	OXY	500	1	3.0308	1.460	0.371
						1.430	0.363
					AVERAGE DISPERSION =		0.367
ERH 23 1	1	UNSINTERED			3.1666	1.770	0.430
						1.680	0.408
					AVERAGE DISPERSION =		0.419
ERH 23 2	1	OXY	500	4	3.1666	1.740	0.423
						1.730	0.421
					AVERAGE DISPERSION =		0.422
ERH 23 3	1	OXY	500	16	3.1666	1.880	0.457
						1.860	0.452
					AVERAGE DISPERSION =		0.455
ERH 46 *	1	OXY	550	1	3.0189	1.490	0.380
						1.500	0.382
					AVERAGE DISPERSION =		0.381
ERH 46 1	1	OXY	550	1	3.1210	1.440	0.355
ERH 46 2	1	OXY	550	4	3.1210	1.510	0.372
						1.410	0.348
					AVERAGE DISPERSION =		0.360
ERH 46 3	1	OXY	550	16	3.1210	1.230	0.303
						1.310	0.323
					AVERAGE DISPERSION =		0.313
ERH 49 *	1	OXY	600	1	3.0165	1.330	0.339
						1.420	0.362
						1.430	0.365
					AVERAGE DISPERSION =		0.356
ERH 50 *	1	OXY	700	1	3.0628	1.160	0.292
						1.210	0.304
					AVERAGE DISPERSION =		0.298
ERH 50 1	1	OXY	700	1	3.1704	1.150	0.279
						1.340	0.325
					AVERAGE DISPERSION =		0.302

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
ERH 50 2	1	OXY	700	4	3.1704	1.160	0.282
						1.210	0.294
					AVERAGE DISPERSION =		0.288
ERH 50 3	1	OXY	700	16	3.1704	0.970	0.236
						0.980	0.238
					AVERAGE DISPERSION =		0.237
ERH 52 *	1	OXY	750	1	3.0676	1.070	0.268
						1.070	0.268
					AVERAGE DISPERSION =		0.268
ERH 15 1	1	UNSINTERED			3.0570	1.950	0.491
						1.920	0.483
					AVERAGE DISPERSION =		0.487
ERH 15 2	1	OXY	800	1	3.0570	0.950	0.239
						0.960	0.242
					AVERAGE DISPERSION =		0.240
ERH 15 3	1	OXY	800	4	3.0570	0.470	0.118
						0.730	0.184
						0.610	0.154
					AVERAGE DISPERSION =		0.152
ERH 15 4	1	OXY	800	16	3.0570	0.430	0.108
						0.380	0.096
					AVERAGE DISPERSION =		0.102
ERH 47 *	1	HYD	550	1	3.0325	1.440	0.366
						1.490	0.378
					AVERAGE DISPERSION =		0.372
ERH 47 1	1	HYD	550	1	3.1358	1.660	0.407
						1.610	0.395
					AVERAGE DISPERSION =		0.401
ERH 47 2	1	HYD	550	4	3.1358	1.580	0.388
						1.540	0.378
					AVERAGE DISPERSION =		0.383
ERH 47 3	1	HYD	550	16	3.1358	1.610	0.395
						1.460	0.358
					AVERAGE DISPERSION =		0.377
ERH 48 *	1	HYD	600	1	3.0634	1.460	0.367
						1.520	0.382
					AVERAGE DISPERSION =		0.374

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
ERH 51 *	1	HYD	700	1	3.0429	1.380	0.349
						1.440	0.364
					AVERAGE DISPERSION =		0.357
ERH 51 1	1	HYD	700	1	3.1421	1.510	0.370
						1.270	0.311
					AVERAGE DISPERSION =		0.341
ERH 28 1	1	UNSINTERED			3.1291	1.620	0.399
						1.780	0.438
					AVERAGE DISPERSION =		0.418
ERH 28 2	1	HYD	700	4	3.1291	1.490	0.367
ERH 28 3	1	HYD	700	16	3.1291	1.370	0.337
						1.280	0.315
					AVERAGE DISPERSION =		0.326
ERH 56 *	1	HYD	800	1	2.4902	0.840	0.260
						0.890	0.275
					AVERAGE DISPERSION =		0.267
ERH 56 1	1	HYD	800	1	2.5713	0.940	0.281
ERH 56 2	1	HYD	800	4	2.5713	0.710	0.213
						0.720	0.216
					AVERAGE DISPERSION =		0.214
ERH 56 3	1	HYD	800	16	2.5713	0.740	0.222
						0.720	0.216
					AVERAGE DISPERSION =		0.219
RH 61A*	2	UNSINTERED			3.0264	2.530	0.322
						2.620	0.333
					AVERAGE DISPERSION =		0.327
RH 84 *	2	OXY	300	1	3.0203	2.420	0.308
						2.480	0.316
					AVERAGE DISPERSION =		0.312
RH 68 *	2	OXY	500	1	3.0514	2.510	0.317
						2.580	0.325
					AVERAGE DISPERSION =		0.321
RH 74 *	2	OXY	600	1	3.0524	2.620	0.330
						2.610	0.329
					AVERAGE DISPERSION =		0.330

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
RH 73 *	2	OXY	700	1	3.0383	2.200	0.279
						2.120	0.269
						2.190	0.277
					AVERAGE DISPERSION =		0.275
RH 72 *	2	OXY	800	1	3.0316	0.630	0.080
						0.590	0.075
					AVERAGE DISPERSION =		0.077
RH 67 *	2	HYD	600	1	3.0840	2.530	0.316
						2.510	0.313
					AVERAGE DISPERSION =		0.314
RH 65 *	2	HYD	700	1	3.0248	2.120	0.270
						2.080	0.265
					AVERAGE DISPERSION =		0.267
RH 65A*	2	HYD	700	1	3.0446	2.060	0.260
						2.020	0.255
					AVERAGE DISPERSION =		0.258
RH 64 *	2	HYD	800	1	3.0262	2.020	0.257
						1.890	0.240
					AVERAGE DISPERSION =		0.249
RH 64A*	2	HYD	800	1	3.0514	1.950	0.246
						1.870	0.236
					AVERAGE DISPERSION =		0.241
2NS *	3	UNSINTERED			2.5204	1.820	0.260
						1.770	0.252
					AVERAGE DISPERSION =		0.256
2NSR *	3	UNSINTERED			2.5291	2.220	0.315
						2.190	0.311
					AVERAGE DISPERSION =		0.313
A *	3	UNSINTERED			2.5247	2.000	0.285
						1.910	0.272
					AVERAGE DISPERSION =		0.278
19 *	3	OXY	500	1	2.5334	4.890	0.694
						4.700	0.667
					AVERAGE DISPERSION =		0.680
19RN *	3	OXY	500	1	2.5586	4.890	0.687
						4.550	0.639
					AVERAGE DISPERSION =		0.663

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
PT 19 1	3	OXY	500	1	2.5155	3.460	0.494
						2.950	0.422
					AVERAGE DISPERSION =		0.458
2RN *	3	OXY	500	16	2.5270	4.840	0.688
						4.420	0.629
					AVERAGE DISPERSION =		0.659
21 *	3	OXY	550	1	2.5405	5.050	0.714
						4.950	0.700
					AVERAGE DISPERSION =		0.707
3 *	3	OXY	550	16	2.5072	4.600	0.659
						4.490	0.644
					AVERAGE DISPERSION =		0.652
3R *	3	OXY	550	16	2.4730	3.160	0.459
3R/2 *	3	OXY	550	16	2.4712	3.260	0.474
3RN *	3	OXY	550	16	2.4898	4.970	0.717
						4.860	0.702
					AVERAGE DISPERSION =		0.710
20 *	3	OXY	600	1	2.5355	4.700	0.666
						4.500	0.638
					AVERAGE DISPERSION =		0.652
PT 20 1	3	OXY	600	1	2.5434	4.130	0.584
						4.220	0.596
					AVERAGE DISPERSION =		0.590
PT 20 2	3	OXY	600	4	2.5434	3.910	0.553
						3.770	0.533
					AVERAGE DISPERSION =		0.543
4 *	3	OXY	600	16	2.5085	3.790	0.543
						3.670	0.526
					AVERAGE DISPERSION =		0.534
10 *	3	OXY	650	1	2.5011	3.030	0.435
						2.840	0.408
					AVERAGE DISPERSION =		0.422
8 *	3	OXY	650	4	2.5617	2.340	0.328
						2.180	0.306
					AVERAGE DISPERSION =		0.317

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
5 *	3	OXY	650	16	2.5101	1.230	0.176
12 *	3	OXY	700	1	2.5097	1.180	0.169
						1.060	0.152
					AVERAGE DISPERSION =		0.160
9 *	3	OXY	700	4	2.5240	0.870	0.124
						0.890	0.127
					AVERAGE DISPERSION =		0.125
7 *	3	OXY	700	16	2.5319	0.790	0.112
7R *	3	OXY	700	16	2.4782	0.730	0.106
C *	3	OXY	800	1	2.5194	0.280	0.040
						0.270	0.039
					AVERAGE DISPERSION =		0.039
PT C 1	3	OXY	800	1	2.1204	0.370	0.063
						0.190	0.032
					AVERAGE DISPERSION =		0.047
PT C 2	3	OXY	800	4	2.1204	0.310	0.053
						0.230	0.039
					AVERAGE DISPERSION =		0.046
KPT 10 1	3	UNSINTERED			2.7912	2.640	0.352
KPT 10 2	3	HYD	600	1	2.7912	2.350	0.314
KPT 10 3	3	HYD	600	4	2.7912	2.290	0.306
						2.350	0.314
					AVERAGE DISPERSION =		0.310
KPT 10 4	3	HYD	600	16	2.7912	1.950	0.260
						1.960	0.262
					AVERAGE DISPERSION =		0.261
KPT 12 1	3	UNSINTERED			2.5826	2.180	0.314
						2.350	0.339
						2.200	0.317
					AVERAGE DISPERSION =		0.324

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
KPT 12 2	3	HYD	700	1	2.5826	1.490	0.215
						1.580	0.228
					AVERAGE DISPERSION =		0.221
KPT 12 3	3	HYD	700	4	2.5826	1.290	0.186
						1.100	0.159
					AVERAGE DISPERSION =		0.172
KPT 12 4	3	HYD	700	16	2.5826	1.050	0.151
						1.050	0.151
					AVERAGE DISPERSION =		0.151
KPT 14 1	3	UNSINTERED			2.6080	2.600	0.371
						2.830	0.404
					AVERAGE DISPERSION =		0.388
KPT 14 2	3	HYD	800	1	2.6080	1.400	0.200
						1.500	0.214
					AVERAGE DISPERSION =		0.207
KPT 14 3	3	HYD	800	4	2.6080	1.450	0.207
						1.480	0.211
					AVERAGE DISPERSION =		0.209
KPT 14 4	3	HYD	800	16	2.6080	1.270	0.181
						0.890	0.127
						0.800	0.114
					AVERAGE DISPERSION =		0.141
D *	3	HYD	600	1	2.5212	1.650	0.235
						1.650	0.235
					AVERAGE DISPERSION =		0.235
PT D 1	3	HYD	600	1	2.2560	2.110	0.336
						2.020	0.322
					AVERAGE DISPERSION =		0.329
PT D 2	3	HYD	600	4	2.2560	1.920	0.306
						1.720	0.274
					AVERAGE DISPERSION =		0.290
PT D 3	3	HYD	600	16	2.2560	1.760	0.280
						1.760	0.280
					AVERAGE DISPERSION =		0.280
18H *	3	HYD	700	1	2.5107	1.350	0.193
						1.340	0.192
					AVERAGE DISPERSION =		0.193

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
PT 18H 1	3	HYD	700	1	2.4541	1.980	0.290
						1.900	0.278
					AVERAGE DISPERSION =		0.284
PT 18H 2	3	HYD	700	4	2.4541	1.220	0.179
						1.260	0.185
					AVERAGE DISPERSION =		0.182
B *	3	HYD	800	1	2.5247	0.730	0.104
						0.810	0.115
					AVERAGE DISPERSION =		0.110
PT AB 1	3	HYD	800	1	2.2502	1.290	0.206
						0.960	0.153
					AVERAGE DISPERSION =		0.180
PT AB 2	3	HYD	800	4	2.2502	0.970	0.155
						0.960	0.153
					AVERAGE DISPERSION =		0.154
PT AB 3	3	HYD	800	16	2.2502	0.470	0.075
						0.490	0.078
					AVERAGE DISPERSION =		0.077
E 23 *	4	UNSINTERED			5.0434	0.670	0.194
						0.680	0.197
					AVERAGE DISPERSION =		0.195
E 97 *	4	UNSINTERED			5.0026	0.750	0.219
						0.770	0.225
					AVERAGE DISPERSION =		0.222
E 24 *	4	OXY	500	1	5.0122	0.960	0.279
						0.890	0.259
					AVERAGE DISPERSION =		0.269
E 28 *	4	OXY	550	1	4.7432	1.010	0.311
						1.010	0.311
					AVERAGE DISPERSION =		0.311
E 25 *	4	OXY	600	1	5.0485	0.870	0.251
						0.900	0.260
						0.910	0.263
					AVERAGE DISPERSION =		0.258
E 27 *	4	OXY	650	1	5.0347	0.590	0.171
						0.600	0.174
					AVERAGE DISPERSION =		0.172

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
E 26 *	4	OXY	700	1	5.0461	0.510	0.147
						0.350	0.101
						0.340	0.098
					AVERAGE DISPERSION =		0.116
E 29A *	4	OXY	800	1	5.0327	0.140	0.041
						0.110	0.032
					AVERAGE DISPERSION =		0.036
E 94 *	4	HYD	600	1	5.0322	0.750	0.217
						0.760	0.220
					AVERAGE DISPERSION =		0.219
E 95 *	4	HYD	700	1	5.0186	0.590	0.172
						0,480	0.140
					AVERAGE DISPERSION =		0.156
E 96 *	4	HYD	800	1	5.0142	0.410	0.119
						0.420	0.122
					AVERAGE DISPERSION =		0.121
IR 62 *	5	UNSINTERED			5.0002	5.710	0.410
						5.790	0.416
					AVERAGE DISPERSION =		0.413
IR 62A*	5	UNSINTERED			5.0560	5.870	0.417
						5.890	0.419
					AVERAGE DISPERSION =		0.418
IR 86 *	5	HYD	600	1	5.0445	5.340	0.381
						5.340	0.381
					AVERAGE DISPERSION =		0.381
IR 86 1	5	HYD	600	1	5.0304	5.100	0.364
						5.200	0.372
					AVERAGE DISPERSION =		0.368
IR 86 2	5	HYD	600	4	5.0304	5.310	0.379
						5.050	0.361
					AVERAGE DISPERSION =		0.370
IR 86 3	5	HYD	600	16	5.0304	5.120	0.366
IR 76 *	5	HYD	700	1	5.0690	5.030	0.357
						5.070	0.360
					AVERAGE DISPERSION =		0.358

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
IR 76 1	5	HYD	700	4	5.0446	4.970	0.354
						4.970	0.354
					AVERAGE DISPERSION =		0.354
IR 76 2	5	HYD	700	16	5.0446	4.840	0.345
						4.720	0.336
					AVERAGE DISPERSION =		0.341
IR 63 *	5	HYD	800	1	5.0124	4.820	0.346
						4.680	0.336
					AVERAGE DISPERSION =		0.341
IR 63 1	5	HYD	800	1	4.9404	4.470	0.325
						4.860	0.354
					AVERAGE DISPERSION =		0.339
IR 63 2	5	HYD	800	4	4.9404	4.440	0.323
						4.670	0.340
					AVERAGE DISPERSION =		0.331
IR 63 3	5	HYD	800	16	4.9404	4.530	0.330
						4.570	0.333
					AVERAGE DISPERSION =		0.331
IR 98 *	5	OXY	300	1	5.0489	6.180	0.440
						6.140	0.437
					AVERAGE DISPERSION =		0.439
IR 98 1	5	OXY	300	1	5.0886	5.870	0.415
						5.620	0.397
					AVERAGE DISPERSION =		0.406
IR 98 2	5	OXY	300	4	5.0886	6.160	0.435
						6.320	0.446
					AVERAGE DISPERSION =		0.441
IR 98 3	5	OXY	300	16	5.0886	6.060	0.428
						6.180	0.437
					AVERAGE DISPERSION =		0.432
IR 107 *	5	OXY	400	1	5.0288	6.880	0.492
						6.810	0.487
					AVERAGE DISPERSION =		0.489
IR 107 1	5	OXY	400	1	5.0787	6.010	0.425
						5.980	0.423
					AVERAGE DISPERSION =		0.424

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
IR 107 2	5	OXY	400	4	5.0787	5.490	0.389
						5.470	0.387
					AVERAGE DISPERSION =		0.388
IR 107 3	5	OXY	400	16	5.0787	2.970	0.210
						3.020	0.214
					AVERAGE DISPERSION =		0.212
IR 87 *	5	OXY	500	1	5.0425	4.460	0.318
						4.580	0.326
					AVERAGE DISPERSION =		0.322
IR 87 1	5	OXY	500	1	5.1051	3.420	0.241
						3.940	0.277
					AVERAGE DISPERSION =		0.259
IR 87 2	5	OXY	500	4	5.1051	2.510	0.177
						2.540	0.179
					AVERAGE DISPERSION =		0.178
IR 87 3	5	OXY	500	16	5.1051	1.220	0.086
						1.470	0.104
					AVERAGE DISPERSION =		0.095
IR 88 *	5	OXY	600	1	5.0244	2.380	0.170
						2.400	0.172
					AVERAGE DISPERSION =		0.171
IR 89 *	5	OXY	700	1	5.0424	0.760	0.054
						0.770	0.055
					AVERAGE DISPERSION =		0.055
IR 89 1	5	OXY	700	1	5.0822	0.730	0.052
IR 89 2	5	OXY	700	4	5.0822	0.190	0.013
						0.180	0.013
					AVERAGE DISPERSION =		0.013
IR 90 *	5	OXY	800	1	5.0437	0.250	0.018
						0.290	0.021
					AVERAGE DISPERSION =		0.019
SIG 20 1	6	UNSINTERED			3.8520	0.980	0.186
						0.710	0.134
					AVERAGE DISPERSION =		0.160
SIG 20 2	6	OXY	550	1	3.8520	0.230	0.044
						0.310	0.059
					AVERAGE DISPERSION =		0.051

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
SIG 20 3	6	OXY	550	4	3.8520	0.440	0.083
						0.280	0.053
					AVERAGE DISPERSION =		0.068
SIG 20 4	6	OXY	550	16	3.8520	0.290	0.055
						0.330	0.063
						0.220	0.042
					AVERAGE DISPERSION =		0.053
SIG 22 1	6	UNSINTERED			3.7419	0.540	0.105
						0.680	0.133
					AVERAGE DISPERSION =		0.119
SIG 22 2	6	OXY	400	4	3.7419	0.670	0.131
						0.660	0.129
					AVERAGE DISPERSION =		0.130
SIG 22 3	6	OXY	400	16	3.7419	0.490	0.096
						0.540	0.105
					AVERAGE DISPERSION =		0.100
SIG 25 1	6	UNSINTERED			3.8374	0.580	0.110
						0.530	0.101
					AVERAGE DISPERSION =		0.106
SIG 25 2	6	OXY	500	1	3.8375	0.580	0.110
						0.590	0.112
					AVERAGE DISPERSION =		0.111
SIG 25 3	6	OXY	500	4	3.8375	0.480	0.091
						0.510	0.097
					AVERAGE DISPERSION =		0.094
SIG 25 4	6	OXY	500	16	3.8375	0.250	0.048
						0.230	0.044
					AVERAGE DISPERSION =		0.046
SIG 27 1	6	UNSINTERED			3.8240	0.850	0.162
						0.730	0.139
					AVERAGE DISPERSION =		0.151
SIG 27 2	6	OXY	460	1	3.8240	0.590	0.113
						0.400	0.076
					AVERAGE DISPERSION =		0.094
SIG 27 3	6	OXY	460	4	3.8240	0.450	0.086
						0.310	0.059
					AVERAGE DISPERSION =		0.073

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
SIG 27 4	6	OXY	460	16	3.8240	0.500	0.095
						0.520	0.099
					AVERAGE DISPERSION =		0.097
SIG 29 1	6	UNSINTERED			3.8852	0.480	0.090
						0.680	0.128
					AVERAGE DISPERSION =		0.109
SIG 29 2	6	OXY	400	1	3.8852	0.700	0.131
						0.660	0.124
					AVERAGE DISPERSION =		0.128
SIG 29 3	6	OXY	400	4	3.8852	0.470	0.088
						0.540	0.101
					AVERAGE DISPERSION =		0.095
SIG 29 4	6	OXY	400	16	3.8852	0.490	0.092
						0.660	0.124
						0.640	0.120
					AVERAGE DISPERSION =		0.112
SIG 31 1	6	UNSINTERED			5.0202	0.980	0.142
						0.700	0.102
						0.550	0.080
					AVERAGE DISPERSION =		0.108
SIG 32 1	6	UNSINTERED			4.9871	0.940	0.138
						0.940	0.138
					AVERAGE DISPERSION =		0.138
SIG 32 2	6	HYD	600	1	4.9871	0.790	0.116
						0.760	0.111
					AVERAGE DISPERSION =		0.113
SIG 32 3	6	HYD	600	4	4.9871	0.370	0.054
						0.550	0.080
					AVERAGE DISPERSION =		0.067
SIG 32 4	6	HYD	600	16	4.9871	0.720	0.105
						0.660	0.097
					AVERAGE DISPERSION =		0.101
SIG 34 1	6	UNSINTERED			4.9685	0.810	0.119
						0.840	0.123
					AVERAGE DISPERSION =		0.121
SIG 34 2	6	HYD	700	1	4.9685	0.110	0.016
						0.160	0.023
					AVERAGE DISPERSION =		0.020

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
SIG 34 3	6	HYD	700	4	4.9685	0.230	0.034
SIG 36 1	6	UNSINTERED			4.9625	0.960	0.141
						0.930	0.137
					AVERAGE DISPERSION =		0.139
SIG 36 2	6	HYD	600	1	4.9625	0.790	0.116
						0.770	0.113
					AVERAGE DISPERSION =		0.115
SIG 36 3	6	HYD	600	4	4.9625	0.510	0.075
						0.750	0.110
						0.510	0.075
					AVERAGE DISPERSION =		0.087
SIG 36 4	6	HYD	600	16	4.9625	0.420	0.062
						0.240	0.035
					AVERAGE DISPERSION =		0.049
SAL 1 1	7	UNSINTERED			5.0007	1.530	0.223
						1.460	0.213
					AVERAGE DISPERSION =		0.218
SAL 1 2	7	OXY	600	1	5.0007	0.570	0.083
						0.410	0.060
					AVERAGE DISPERSION =		0.071
SAL 1 3	7	OXY	600	16	5.0007	0.140	0.020
						0.200	0.029
					AVERAGE DISPERSION =		0.025
SAL 2 1	7	UNSINTERED			5.0001	1.660	0.242
						1.070	0.156
					AVERAGE DISPERSION =		0.199
SAL 2 2	7	OXY	600	1	5.0001	0.240	0.035
						0.660	0.096
					AVERAGE DISPERSION =		0.066
SAL 2 3	7	OXY	600	16	5.0001	0.350	0.051
						0.350	0.051
					AVERAGE DISPERSION =		0.051
SAL 3 1	7	UNSINTERED			4.9975	1.850	0.270
						1.230	0.180
					AVERAGE DISPERSION =		0.225

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
SAL 3 2	7	OXY	550	1	4.9975	0.960	0.140
						0.610	0.089
					AVERAGE DISPERSION =		0.115
SAL 3 3	7	OXY	550	16	4.9975	0.460	0.067
SAL 4 1	7	OXY	500	1	4.9403	1.710	0.253
						1.420	0.210
					AVERAGE DISPERSION =		0.231
SAL 4 2	7	OXY	500	16	4.9403	0.980	0.145
						0.940	0.139
					AVERAGE DISPERSION =		0.142
SAL 16 1	7	UNSINTERED			5.0011	1.080	0.158
						0.800	0.117
					AVERAGE DISPERSION =		0.137
SAL 16 2	7	OXY	400	1	4.9960	1.040	0.152
						0.990	0.145
					AVERAGE DISPERSION =		0.148
SAL 16 3	7	OXY	400	4	4.9960	0.990	0.145
						0.950	0.139
					AVERAGE DISPERSION =		0.142
SAL 16 4	7	OXY	400	16	4.9960	1.020	0.149
						0.950	0.139
					AVERAGE DISPERSION =		0.144
SAL 22 1	7	UNSINTERED			5.0304	1.110	0.161
						1.070	0.155
					AVERAGE DISPERSION =		0.158
SAL 22 2	7	OXY	450	1	5.0304	1.030	0.149
						0.900	0.131
					AVERAGE DISPERSION =		0.140
SAL 22 3	7	OXY	450	4	5.0304	0.680	0.099
						0.920	0.133
						0.660	0.096
					AVERAGE DISPERSION =		0.109
SAL 22 4	7	OXY	450	16	5.0304	0.900	0.131
						0.670	0.097
					AVERAGE DISPERSION =		0.114

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
SAL 25 1	7	UNSINTERED			4.9895	0.920	0.135
						0.980	0.143
					AVERAGE DISPERSION =		0.139
SAL 25 2	7	HYD	600	1	4.9895	0.690	0.101
						0.670	0.098
					AVERAGE DISPERSION =		0.099
SAL 25 3	7	HYD	600	4	4.9895	0.340	0.050
						0.610	0.089
					AVERAGE DISPERSION =		0.069
SAL 25 4	7	HYD	600	16	4.9895	0.280	0.041
						0.230	0.034
					AVERAGE DISPERSION =		0.037
SAL 27 1	7	UNSINTERED			5.0119	0.970	0.141
						0.910	0.132
					AVERAGE DISPERSION =		0.137
SAL 27 2	7	HYD	700	1	5.0119	0.420	0.061
						0.240	0.035
					AVERAGE DISPERSION =		0.048
SAL 27 3	7	HYD	700	4	5.0119	0.320	0.047
						0.360	0.052
					AVERAGE DISPERSION =		0.049
SAL 29 1	7	UNSINTERED			4.9863	1.030	0.151
						0.960	0.140
					AVERAGE DISPERSION =		0.146
SAL 29 2	7	OXY	500	1	4.9863	0.540	0.079
						0.630	0.092
					AVERAGE DISPERSION =		0.086
SAL 29 3	7	OXY	500	4	4.9863	0.500	0.073
						0.490	0.072
					AVERAGE DISPERSION =		0.072
SAL 29 4	7	OXY	500	16	4.9863	0.350	0.051
						0.350	0.051
					AVERAGE DISPERSION =		0.051
GAL 11 1	8	UNSINTERED			4.9829	2.930	0.429
						2.930	0.429
					AVERAGE DISPERSION =		0.429

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
GAL 11 2	8	HYD	600	1	4.9829	2.620	0.384
						2.520	0.369
					AVERAGE DISPERSION =		0.376
GAL 11 3	8	HYD	600	4	4.9829	2.570	0.376
						2.540	0.372
					AVERAGE DISPERSION =		0.374
GAL 11 4	8	HYD	600	16	4.9829	2.070	0.303
						2.170	0.318
					AVERAGE DISPERSION =		0.310
GAL 16 1	8	UNSINTERED			4.7618	1.760	0.270
						1.850	0.283
					AVERAGE DISPERSION =		0.277
GAL 16 2	8	OXY	500	1	4.7618	2.750	0.421
						2.630	0.403
					AVERAGE DISPERSION =		0.412
GAL 16 3	8	OXY	500	4	4.7618	2.910	0.446
						2.950	0.452
					AVERAGE DISPERSION =		0.449
GAL 16 4	8	OXY	500	16	4.7618	2.760	0.423
						3.020	0.463
					AVERAGE DISPERSION =		0.443
GAL 18 1	8	UNSINTERED			4.7551	1.780	0.273
						1.630	0.250
					AVERAGE DISPERSION =		0.262
GAL 18 2	8	OXY	500	1	4.7551	3.690	0.566
						3.590	0.551
					AVERAGE DISPERSION =		0.559
GAL 18 3	8	OXY	500	4	4.7551	3.170	0.486
						3.060	0.470
					AVERAGE DISPERSION =		0.478
GAL 18 4	8	OXY	500	16	4.7551	3.400	0.522
						3.500	0.537
					AVERAGE DISPERSION =		0.529
GAL 20 1	8	UNSINTERED			4.7031	1.660	0.258
						1.980	0.307
						1.470	0.228
					AVERAGE DISPERSION =		0.264

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
GAL 20 2	8	OXY	450	1	4.7031	2.050	0.318
						2.080	0.323
					AVERAGE DISPERSION =		0.320
GAL 20 3	8	OXY	450	4	4.7031	2.710	0.420
						2.570	0.399
					AVERAGE DISPERSION =		0.410
GAL 20 4	8	OXY	450	16	4.7031	3.170	0.492
						2.950	0.458
					AVERAGE DISPERSION =		0.475
GAL 24 1	8	UNSINTERED			4.7454	1.740	0.268
						1.430	0.220
						1.360	0.209
					AVERAGE DISPERSION =		0.232
GAL 24 2	8	OXY	600	1	4.7454	2.150	0.331
						2.200	0.338
					AVERAGE DISPERSION =		0.334
GAL 24 3	8	OXY	600	4	4.7454	1.730	0.266
						1.220	0.188
						1.420	0.218
					AVERAGE DISPERSION =		0.224
GAL 24 4	8	OXY	600	16	4.7454	1.010	0.155
						1.060	0.163
					AVERAGE DISPERSION =		0.159
GAL 26 1	8	UNSINTERED			4.7475	2.220	0.341
						2.350	0.361
					AVERAGE DISPERSION =		0.351
GAL 26 2	8	OXY	700	1	4.7475	0.800	0.123
						0.820	0.126
					AVERAGE DISPERSION =		0.124
GAL 26 3	8	OXY	700	4	4.7475	0.310	0.048
						0.230	0.035
					AVERAGE DISPERSION =		0.041
GAL 28 1	8	UNSINTERED			4.7522	2.050	0.315
						2.090	0.321
					AVERAGE DISPERSION =		0.318
GAL 28 2	8	OXY	800	1	4.7522	0.560	0.086
						0.480	0.074
					AVERAGE DISPERSION =		0.080

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
GAL 30 1	8	UNSINTERED			4.7222	1.680	0.260
						2.050	0.317
						1.160	0.179
					AVERAGE DISPERSION =		0.252
GAL 30 2	8	OXY	400	1	4.7222	1.990	0.307
						1.530	0.236
					AVERAGE DISPERSION =		0.272
GAL 30 3	8	OXY	400	4	4.7222	1.980	0.306
						1.800	0.278
					AVERAGE DISPERSION =		0.292
GAL 30 4	8	OXY	400	16	4.7222	1.780	0.275
						1.860	0.287
					AVERAGE DISPERSION =		0.281
GAL 32 1	8	UNSINTERED			4.9893	1.450	0.212
						1.420	0.208
					AVERAGE DISPERSION =		0.210
GAL 32 2	8	HYD	600	1	4.9893	1.230	0.180
						1.310	0.192
					AVERAGE DISPERSION =		0.186
GAL 32 3	8	HYD	600	4	4.9893	1.660	0.243
						1.700	0.249
					AVERAGE DISPERSION =		0.246
GAL 32 4	8	HYD	600	16	4.9893	1.680	0.246
						1.710	0.250
					AVERAGE DISPERSION =		0.248
GAL 34 1	8	UNSINTERED			5.0061	1.910	0.278
						2.000	0.291
					AVERAGE DISPERSION =		0.285
GAL 34 2	8	HYD	700	1	5.0061	1.630	0.238
						1.650	0.240
					AVERAGE DISPERSION =		0.239
GAL 34 3	8	HYD	700	4	5.0061	1.490	0.217
						1.020	0.149
					AVERAGE DISPERSION =		0.183
GAL 34 4	8	HYD	700	16	5.0061	1.230	0.179
						1.200	0.175
					AVERAGE DISPERSION =		0.177

RUN	CAT	PRETREATMENT ATM	TEMP (C)	TIME (HR)	SAMPLE SIZE (GM)	NUMBER OF PULSES ADSORBED	DISP
GAL 36 1	8	UNSINTERED			4.9884	1.390	0.203
						2.060	0.301
						1.650	0.241
					AVERAGE DISPERSION =		0.249
GAL 36 2	8	HYD	800	1	4.9884	1.020	0.149
						1.060	0.155
					AVERAGE DISPERSION =		0.152
GAL 36 3	8	HYD	800	4	4.9884	1.030	0.151
						1.140	0.167
					AVERAGE DISPERSION =		0.159
GAL 36 4	8	HYD	800	16	4.9984	0.780	0.114
						0.810	0.118
					AVERAGE DISPERSION =		0.116

TABLE B-3 Program SINTER

```
C     *****
CC     THIS PROGRAM CALCULATES THE METAL DISPERSION,BASED ON ADSORPTION
CC       UPTAKES, FOR SINTERING EXPERIMENTS CONDUCTED BY BHARAT CHAHAR
C     *****
C
C     DATA INPUT
C
C     ONE DATA CARD PER RUN
C
C     CN IS THE WEIGHT % METAL
C
C
C     THE DATA IN COLUMNS 7 TO 30 CONSISTS OF ALPHAMERIC INPUT
C       COLUMNS 7 TO 14 - RUN IDENTIFICATION
C       COLUMNS 15 TO 18 - CATALYST IDENTIFICATION
C       COLUMNS 20 TO 22 - SINTERING ATMOSPHERE
C       COLUMNS 24 TO 26 - SINTERING TEMPERATURE IN DEG. C
C       COLUMNS 28 TO 30 - SINTERING TIME IN HOURS
C
C     W, THE WEIGHT OF THE CATALYST SAMPLE IN GRAMS, IS
C      READ FROM COLUMNS 35 TO 40
C
C     P(I) IS READ FROM COLUMNS 41 TO 65  (I HAS A MAX VALUE OF 5)
C      P(I) IS THE UPTAKE FOR W GRAMS OF CATALYSTS IN PULSES OF HYDROGEN
C      IF LESS THEN 5 DETERMINATIONS OF UPTAKE WERE CARRIED OUT (THE
C       USUAL CASE) THEN THE I+1 ENTERY SHOULD BE A NEGATIVE NUMBER
C
C     THE FORMAT FOR THE DATA INPUT IS  1F6.3,7A4,1F7.4,5F5.2
```

... cont'd

```
      DIMENSION P(5),D(5)
      DATA B/'IR  '/
      DATA Q/'IR 1'/
      DATA C/'RH  '/
      DATA G/'ERH '/
      NLINE =0
     WRITE(6,100)
      WRITE(6,101)
      WRITE(6,102)
  100 FORMAT(1H1,////,27X,'PRETREATMENT    SAMPLE   NUMBER')
  101 FORMAT(10X,'RUN        CAT   ATM TEMP TIME     SIZE   OF PULSES
     1  DISP')
  102 FORMAT(30X,'(C)  (HR)      (GM)   ADSORBED')
      U=18.7
C     U IS THE NUMBER OF MICROMOLES OF HYDROGEN PER PULSE
  200 CONTINUE
     READ(5,103) CN,Z1,Z2,Z3,Z4,Z5,Z6,Z7,W,(P(I),I=1,5)
  103 FORMAT(1F6.3,7A4,1F7.4,5F5.2)
      DO 203 NI=1,5
      IF(P(NI))202,202,203
  203 NP=NI
C     NP IS THE NUMBER OF ADSORPTION DONE PER RUN (POSITIVE VALUES OF P(I))
  202 CONTINUE
C
C     F IN THE FOLLOWING STATEMENTS IS THE NUMBER OF MICRO-GRAM-ATOMS
C       OF METAL PER GRAM OF CATALYST FOR THE VARIOUS CATALYSTS
C     F = (PER CENT METAL)/(100)/(ATOMIC WT OF METAL)*10**6
C
      IF(Z1.EQ.B) GO TO 150
      CONTINUE
```

...cont'd

```
      IF(Z1.EQ.Q) GO TO 150
      CONTINUE
      IF(Z1.EQ.C) GO TO 140
      CONTINUE
      IF(Z1.EQ.G) GO TO 140
      F=CN/0.019509
      GO TO 160
 140  F=CN/0.010291
      GO TO 160
 150  F=CN/0.019222
C
C     D(I) IS THE CALCULATED METAL DISPERSION FOR THE I'TH ADSORPTION
C     D(I) = (NUMBER OF PULSES)(MICROMOLES OF HYDROGEN PER PULSE(2.0)/
C            (MICRO-GRAM-ATOMS OF METAL IN SAMPLE  )
C     D(I) = (P(I))*(U)*(2.0)/F/W
C
 160 DT=0.0
      DO 301 I=1,NP
      D(I)=P(I)*U*2.0/F/W
      DT=DT+D(I)
 301  CONTINUE
      CNP=NP
      DAVG=DT/CNP
C
C     DAVG IS THE AVERAGE DISPERSION OF NP DETERMINATIONS
C
      WRITE(6,302)Z1,Z2,Z3,Z4,Z5,Z6,Z7,W,P(1),D(1)
 302  FORMAT( /,9X,2A4,2X,A4,2X,4A4,1X,1F7.4,3X,1F6.3,5X,1F6.3)
      IF(NP-1)306,306,307
 307  CONTINUE
```

...cont'd

```
      WRITE(6,303) (P(I),D(I),I=2,NP)
303   FORMAT(52X,1F6.3,5X,1F6.3)
      WRITE(6,304) DAVG
304   FORMAT(  43X,'AVERAGE DISPERSION =',1F6.3)
306   CONTINUE
      NLINE=NLINE+NP+2
      IF(48-NLINE)305,305,200
305   WRITE(6,100)
      WRITE(6,101)
      WRITE(6,102)
      NLINE=0
      GO TO 200
308   STOP
      END
```